Recovery of humic-like susbtances from low quality composts

Maria Elisabete F. Silva [a,b,c,*], Luís T. Lemos [a], Margarida M.S.M. Bastos [b], Olga C. Nunes [b], Ana C. Cunha-Queda [c]

[a] Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Viseu, Portugal
[b] LEPAE, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Portugal
[c] UIQA, Instituto Superior de Agronomia, Universidade Técnica de Lisboa (TULisbon), Portugal

ABSTRACT

The quality of four commercial composts produced from poultry litter and municipal solid wastes was assessed based on their physic-chemical, stability and maturity parameters. These properties varied among the analysed composts; it was found that electric conductivity, heavy metals content and maturity were the parameters that limited the composts quality. Therefore, the feasibility of using them to obtain liquid fertilisers rich in humic-like substances (HS) was assessed. The HS yield, phytotoxicity, heavy metals co-extraction and chemical characterization were carried out. The linkage of the HS chemical composition with the compost properties was assessed by multivariate analysis. Among the compost properties, germination indices, Cr and Cu contents were the parameters that correlated most with the HS chemical composition. The low levels of metals and absence of phytotoxicity in all the analysed HS extracts indicate that composts with low quality may be used to produce liquid organic fertilisers, substituting those from natural resources.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Composting represents a strategy of organic waste treatment that is fully compatible with sustainable agriculture given compost term application may counteract depletion of organic matter in soils (Albrecht et al., 2011). Indeed, the utilisation of compost in agriculture management is expected to enrich the soil in mature organic material rich in humic-like substances (HS), which contributes to the health and fertility of soils (Senesi et al., 1996). However, to assure that the introduction of compost in the agriculture soils does not have harmful effects, composts must have high quality.

Compost quality refers to the overall state of compost in regard to physical, chemical and biological characteristics (Lasaridi et al., 2006). Parameters as electrical conductivity, ammonium nitrogen and the presence of heavy metals in composts are among the factors that can reduce their quality and may limit their application to soil. Therefore, in an attempt to avoid negative impacts due to the utilisation of low quality composts, the upper limits of these parameters are regulated by national (Anonymous, 2008) and international (DG ENV.A.2, 2001) quality proposal guidelines.

The utilisation of composts with low quality, i.e., those not following the national and/or international quality proposal guidelines, namely in heavy metals content, as a source of HS may be a sustainable alternative to their usage as soil conditioners. Indeed, nowadays there is a growing tendency to use humic substances as liquid organic amendment, produced from natural resources such as leonardite, peat, and lignite (IHSS, 2008; Tahir et al., 2011) but their use can contribute to the extinction of these natural resources. The most common method to extract HS from these natural resources involves alkaline extraction (e.g., NaOH) followed by precipitation at low pH. Salts are further removed by procedures such as cation exchange or dialysis. With this methodology, all the extracted organic acids are expected to be present in either the humic acid or fulvic acid fraction (IHSS, 2008). Pyrophosphate (e.g., $Na_4P_2O_7$) is also efficient on HS extraction (e.g., Donisa et al., 2003), although lower HS yields are obtained than with strong alkaline extraction (Stevenson, 1982). Nevertheless, the utilisation of mild reagents such as $Na_4P_2O_7$ over strong alkali reagents may be advantageous since the latter may alter the chemical composition of HS constituents (Prentice and Webb, 2010). Inevitably, heavy metals present in the raw material are co-extracted with HS, predominantly with the fulvid acids (Borůvka and Drábek, 2004; Donisa et al., 2003; Hsu and Lo, 2001).

In the present study, the quality of four Portuguese commercial composts was assessed based on their physic-chemical, stability and maturity parameters. The feasibility of using these composts to obtain liquid fertilisers rich in humic-like substances was also

* Corresponding author at: Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Viseu, Campus Politécnico de Repeses, 3504-510 Viseu, Portugal. Tel.: +351 232480500; fax: +351 232424651.
E-mail address: beta@estv.ipv.pt (Maria Elisabete F. Silva).

assessed. The HS yield, heavy metals co-extraction, and HS chemical characterization were determined. A multivariate analysis permitted to correlate the HS chemical composition with the physic-chemical, stability and maturity parameters of the respective composts.

2. Methods

2.1. Composts

Four types of Portuguese commercial composts were chosen based on the characteristics of the raw materials and their type of collection. The operational parameters of these composts are described in Table 1.

2.2. Physic–chemical characterization of composts

The pH, electrical conductivity, moisture, organic matter, total carbon, total nitrogen and NH_4^+–N content of compost samples were determined according to standard procedures, as reported by Silva et al. (2009). All the analyses were performed in triplicates.

2.3. Extraction of humic-like substances

Extraction and fractionation of humic-like substances (HS) were carried out according to the methodology described in the Spanish official method for the analysis of fertilising organic products (R.D. 1110/12, July 1991), which consists of successive treatments of the compost with an alkaline solvent. The humic-like substances extract (HE) was obtained by shaking 10 g dry compost with 120 mL of 0.1 M pyrophosphate–KOH (pH 13) for 1 h. After centrifugation for 20 min at 4000 rpm, the supernatant and the precipitate (residue) were carefully separated; this operation was repeated three times and the dark-coloured supernatants were pooled, allowed to settle overnight, and centrifuged for 20 min at 4000 rpm. The resultant HE was fractionated by ~1.5 mL 96% H_2SO_4 addition (pH 2). After 24 h at room temperature and centrifugation for 20 min at 4000 rpm, the insoluble fraction, which contained humic-like acid substances (HA fraction), was separated from the soluble fulvic-like acid substances (FA fraction). HA was dissolved in distilled water. The total organic carbon (TOC) content of HE, HA and FA was determined by dichromate oxidation and sulphuric acid (Yeomans and Bremner, 1988). It involves a digestion of the sample with an acidified dichromate ($K_2Cr_2O_7$–H_2SO_4) solution and the estimation of the unreacted dichromate by titration of the cooled digest with an acidified solution of ferrous ammonium sulphate. Results were expressed as the percentage of total organic carbon of the parent compost in each fraction (HEC, HAC and FAC). The humification indices were calculated using the following expressions (Roletto et al., 1985):

$$\text{Degree of polymerization (DP)} = \text{HAC/FAC} \tag{1}$$

$$\text{Humification ratio (HR)} = 100 \times \text{HEC/TOC} \tag{2}$$

$$\text{Humification index (HI)} = 100 \times \text{HAC/TOC} \tag{3}$$

$$\text{Percentage of humic acids (PHA)} = 100 \times \text{HAC/HEC} \tag{4}$$

The HE, HA and FA fractions were further purified by dialysis (Spectra-Por membrane 1000 Da) until the electric conductivity was below 1 mS cm^{-1} (Amir et al., 2005). The HA and FA fractions were finally freeze-dried.

2.4. Humic-like substances chemical characterization

The functional groups of HA and FA fractions were identified by Fourier transform infrared (FT-IR) and magnetic resonance (NMR) spectroscopy. FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer using KBr pellets (2 mg sample: 200 mg KBr). ^{13}C-NMR spectra with ^{1}H broadband decoupling and ^{1}H NMR were recorded at 100.63 MHz on a Bruker Avance III 400 Spectrometer. The solution was prepared by dissolving 25 mg of HA or 10 mg of FA in 500 μl of 0.3 M NaOD/D$_2$O, gently shacked overnight, centrifuged at 10000 rpm for 15 min and filtered through glass wool into NMR tubes. A commercial HA (Aldrich) was included as a control. Acquisition time was 1.3 s, relaxation delay was 5 s with a pulse of 30° and the total acquisition time was 63 h. Free induction decays were processed by applying 50 Hz line broading and baseline corrections. The total area of each ^{13}C-NMR spectrum was integrated and divided into the following regions: 0–55, 55–110, 110–165, 165–200 ppm (Jouraiphy et al., 2008) and 200–220 ppm (Tanaka, 2012). Integral regions for ^{1}H-NMR spectra were selected as follows: 0.30–2.05, 2.05–3.10, 3.10–4.20 and 5.60–9.00 ppm (Guéguen et al., 2012).

2.5. Heavy metals content in composts and humic-like substances thereof

The content in Zn, Cu, Ni, Cd, Cr and Pb was determined in the HE, HA and FA fractions, in the residue and in the parent compost by flame atomic absorption spectrophotometry (Perkin–Elmer Atomic Absorption Spectrophotometer) after digestion of the samples with "aqua regia", followed by filtration (EN 13650, 2001).

2.6. Stability and maturity of composts and humic-like substances thereof

The stability was assessed using the Dewar self-heating test and the respiration activity after 4 days (AT4). In Dewar self-heating test the ability of the compost material to reheat was evaluated. Vessels (1.5 L) were filled with compost samples with a standardized moisture content of 35% (Laga-Merkblatt M10, 1995). Temperature evolution was measured until heat production had ceased. According to Laga-Merkblatt M10 (1995), the degree of stability was attributed by taking into account the maximum temperature reached in each vessel: degree I –temperature >60 °C; degree II – temperature between 50 and 60 °C; degree III –temperature between 40 and 50 °C; degree IV –temperature between 30 and 40 °C; degree V –temperature <30 °C. Respiration activity after 4 days (AT4) was carried out according to DIN 19737 (2001) methodology.

Maturation was evaluated using the humification indices described above and phytotoxicity. The phytotoxicity was assessed through germination tests with the aqueous extract obtained from the parent compost and with the humic-like substances extract (HE) thereof using a modification of the procedure described by Tiquia et al. (1996). A leonardite based commercial liquid fertiliser (Humistar®) was included as a control. Approximately 10 g dry compost was mixed with sterile distilled water at a 1:10 (w/V) ratio, and stirred for 1 h at room temperature. The slurry was then filtered under vacuum using a 2 μm paper filter (Schleicher&Schuell). Approximately 3 mL of compost aqueous extract or dialysed HE was added on a Petri dish containing 7 seeds of cress (*Lepidium sativum* L.). All HE and the commercial liquid fertiliser were diluted to obtain the same HS concentration (0.5 mg L^{-1}). Each extract was assayed seven times. Controls were prepared with sterile distilled water. After incubation at 27 °C for 2 days, germination index (GI) was calculated based on the following formula (Zucconi et al., 1981):