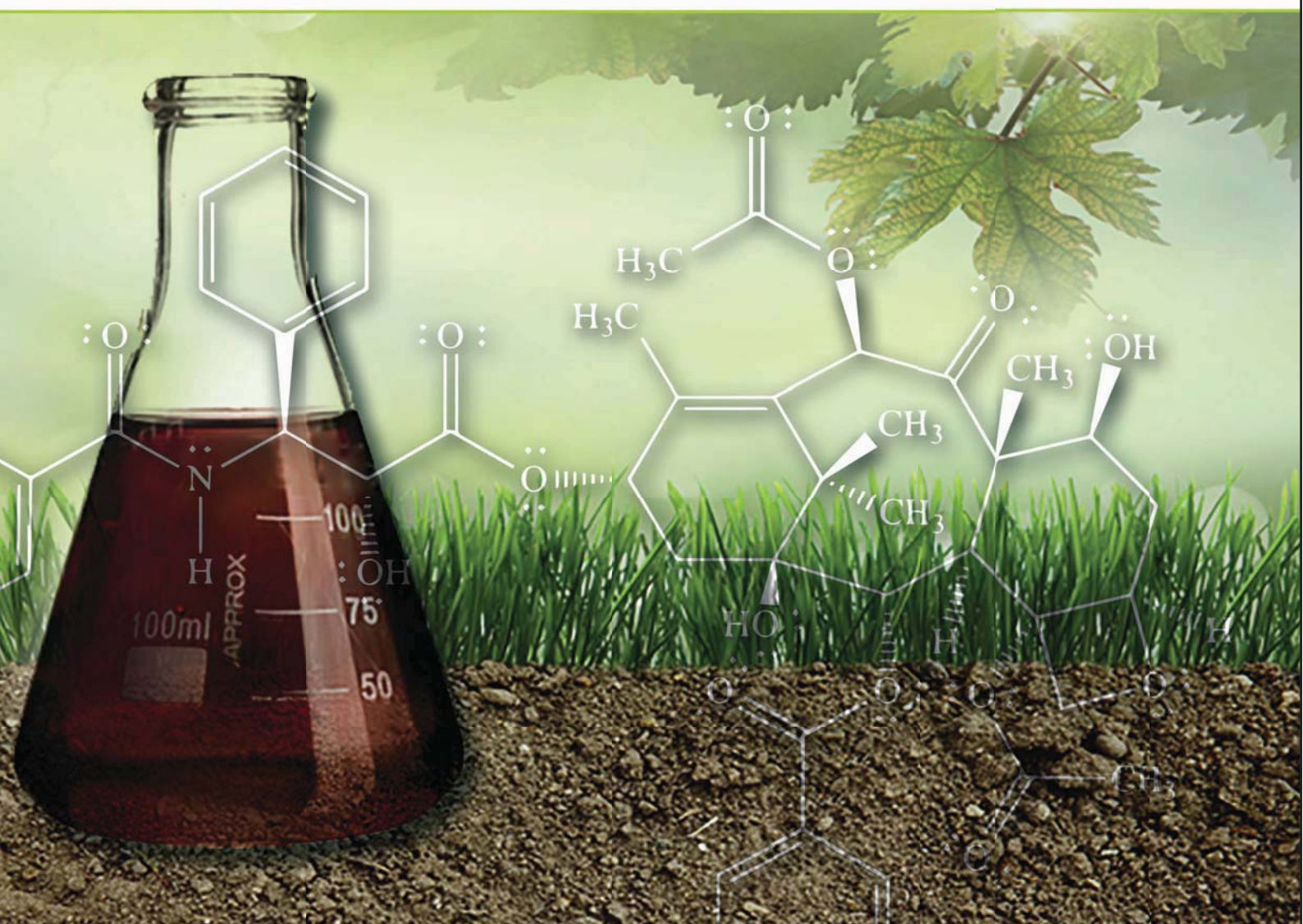


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Humic Substances and Their Contribution to the Climate Change Mitigation



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Effects of percolate recirculation frequency on the organic matter composition after solid-state anaerobic digestion of straw and pig slurry

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Abstract. Restoring humus in soil represents a key factor for improving soil quality. Digestates from anaerobic digestion (AD) can be successfully applied as soil amendments. Here, we investigated changes of the organic matter (OM) composition of digestates from solid-state anaerobic digestion (AD) of straw and pig slurry at different percolate recirculation frequency. Atomic ratios, thermostability indexes, O-alkyl C/alkyl C ratio and Py-GC/MS results consistently showed a positive effect of the highest number (4) of percolate recirculations per day on OM features, resulting in a more stable OM in digestate.

Introduction

AD technologies allow converting organic residues into biogas and digestate, thus recycling materials and replacing energy from fossil fuels with renewable energy. Digestate has been proven to be a good soil amendment [1], useful to restore OM in soil. As such, digestate should consist of stabilized OM to avoid phytotoxicity, greenhouse gases and odorous emissions, and nutrient losses.

In the present study, we investigated changes of the OM composition of digestates obtained from solid-state anaerobic digestion (SS-AD) of straw and pig slurry at different percolate recirculation frequency. Percolate (*i.e.* the liquid fraction of digestate) recirculation was performed to minimize inhibition phenomena during SS-AD, as it could promote the solubilization and leaching of certain inhibitory organic compounds (*i.e.* volatile fatty acids, [2]). The initial mixture and digestate samples were analyzed by elemental analysis (CHNS-O), pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS), thermogravimetric analysis (TGA) and cross polarization magic angle spinning ¹³C nuclear magnetic resonance (CPMAS ¹³C NMR) spectroscopy.

Materials and methods

Experimental set-up. The experiments were performed in 3 polyethylene reactors of 15 L capacity equipped with a percolate recycling system. The initial mixture was composed of pig slurry and straw (3:1 w/w); the inoculum, was added at the same amount of pig slurry to the initial mixture along with 2 L of demineralized water. Percolate leaching through the mixture was collected at the reactor bottom and recycled by the system. Three tests were carried out using 1, 2 and 4 recirculations per day, producing digestate samples *1SS-AD*, *2SS-AD* and *4SS-AD*, respectively. A control test (*i.e.* without percolate recirculation) was also performed, producing digestate *control*.

Elemental analysis. The elemental composition (CHNS-O) was determined in triplicate by flash combustion, using sulfanilic acid as standard; results were expressed as C/N, H/C and O/C ratios.

Py-GC/MS. The analysis was performed using a double-shot pyrolyzer attached to a gas chromatograph. Samples (1–2 mg) were introduced into a pre-heated furnace at 400°C for 1 min and the evolved gases directly injected into the GC/MS. The GC was equipped with a low-polarity fused silica capillary column and used helium as carrier gas at a flow rate of 1 mL min⁻¹. Mass spectra were acquired with a mass selective detector at 70 eV ionizing energy. The identification of individual compounds was achieved by single ion monitoring (SIM), low-resolution mass spectrometry and comparison with stored (NIST and Wiley libraries) and previously published data [3, 4]. The relative abundance of each pyrolysis product was expressed as a percentage (%) of the total chromatogram area, after peak integration.

TGA. About 20 mg sample were heated from 30 to 830°C at 30°C min⁻¹ at a flow rate of 30 mL min⁻¹ synthetic air. Weight loss (%) was calculated within the temperature ranges 250–350°C (WL1) and 350–550°C (WL2). The temperature at which 50% (TG-T₅₀) of the mass loss occurred was also calculated as well as the ratio WL2/WL1, as they are sensitive to OM changes due to biological processes [5, 6].

CPMAS ¹³C NMR spectroscopy. The solid-state ¹³C NMR spectra were obtained by collecting over 5000 scans sample⁻¹ with a Bruker Avance III HD 400 MHz and using zirconium rotors of 4 mm OD. The cross polarization magic angle spinning (CPMAS) technique was applied during magic-angle spinning of the rotor at 14 kHz. A ramped ¹H-pulse was applied during a contact time of 1 ms. The ¹³C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.08 ppm). Spectra were quantified by integration of the following chemical shift regions: alkyl C (0–45 ppm), N-alkyl/methoxyl C (45–60 ppm), O-alkyl C (60–110

ppm), aromatic C (110-140 ppm), O-substituted aromatic C (140-160 ppm) and carboxyl/amide C and carbonyl C (160-220 ppm). The relative abundance of each typical C resonance region was expressed as relative percentage of the total C resonance area (assumed to be 100%) [7].

Results and Discussion

Elemental analysis. When compared with the initial mixture, all digestate samples showed: (i) a decrease of the C/N ratio, particularly for 2SS-AD and 4SS-AD; and (ii) a decrease of the O/C ratio, with the lowest value found for 4SS-AD, which is in line with the lowest content of O-containing functional groups of this sample. Both ratios suggested that the most efficient OM degradation had been attained using 4 percolate recirculations per day.

Py-GC/MS. The identified pyrolysis products were grouped into 7 families, *i.e.* aromatics (Ar), lignin-derived compounds (Lig-), polysaccharide-derived compounds (Ps-), N-compounds (N), ketones, *n*-alkane/*n*-alk-1-ene doublets and alkanols (AKA), *n*-alkanoic acids (FA) and sterols and terpenoids (ST).

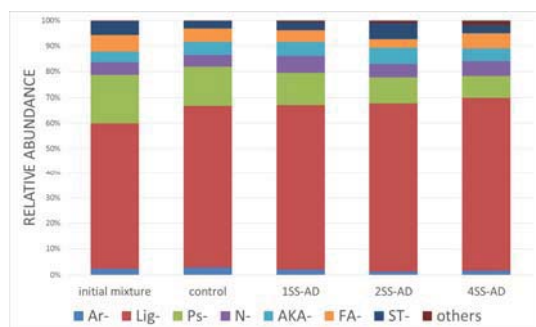


Figure 1. Changes in the relative abundance (%) of the chemical families identified by Py-GC/MS.

As compared to the initial mixture, all digestate samples showed a decrease in Ps-derived compounds and a relative increase in Lig-derived compounds. Increasing percolate recirculation frequency resulted in: (i) a major decrease in Ps-derived compounds (4SS-AD < 2SS-AD < 1SS-AD < control); (ii) a greater relative increase in Lig-derived compounds (the highest in 4SS-AD; Fig. 1). The lower content of more labile organic compounds in digestates (the lowest for 4SS-AD) reflect a higher OM stability (the highest for 4SS-AD).

The third most abundant chemical compound class (13-16%) comprises lipids-derived compounds, including AKA, ST and FA (Fig. 1). Extracting the ion chromatogram *m/z* 74, fatty acids methyl esters (FAMES) distribution among samples was studied. A marked decrease in L-FAMES (C_{21} - C_{30}) was observed in digestate samples with respect to the initial mixture. An opposite trend was found for S-FAMES (C_{13} - C_{20}). These results indicate that AD promoted a chain shortening with L- to S-FAMES conversion (*i.e.* by chain cracking during SS-AD).

TGA. The initial mixture showed *ca.* 51% of WL1. Because of carbohydrates consumption during AD, WL1 decreased with digestion, reaching its minimum value in 4SS-AD (35%). In the initial mixture, control and 1SS-AD, WL2 contributed with 33% to the total weight loss. WL2 increased slightly only in 2SS-AD and 4SS-AD. These results indicate that AD has caused a decrease of the more labile fraction of OM and a relative enrichment of the more stable one. This is in particular evident after increasing percolate recirculation frequency to 4 times per day, in agreement with Py-GC/MS results. The thermostability index WL2/WL1 enhanced from 0.6 in the initial mixture to a maximum of 1 in 4SS-AD. Also TG- T_{50} increased in all digestate samples with increasing percolate recirculation frequency, reaching the highest value in 4SS-AD (424°C). Based on thermostability indexes, 4SS-AD shows the highest recalcitrance to thermal degradation compared to the other digestate samples.

CPMAS ^{13}C NMR spectroscopy. All samples showed high contents of O-alkyl C, commonly ascribed to carbohydrates. Their relative abundance decreased from about 70% in the initial mixture to 55% in the control, and 59, 55 and 48% in 1SS-AD, 2SS-AD and 4SS-AD, respectively, which agrees result shown by Py-GC/MS. Digestate samples also showed a relative increase in the alkyl C contribution, with the highest value in 4SS-AD. As a result, O-alkyl C/alkyl C ratio decreased in the digestates. This ratio, used as an index of the extent of OM decomposition, shows the lowest value in 4SS-AD, confirming a greater degree of OM stability with increasing the percolate recirculation frequency, which is in line with Py-GC/MS and TGA results.

The overall results showed a positive effect of 4 percolate recirculations per day on the OM stability of digestate, in terms of relative increase of the recalcitrant Lig domain at the expenses of the more labile Ps content, suggesting a great potential of 4SS-AD to be successfully used as soil amendment.

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