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Valorization of a pharmaceutical organic sludge through different composting treatments

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ABSTRACT

Nowadays, the agricultural reuse of pharmaceutical sludge is still limited due to environmental and agronomic issues (e.g. low stabilization of the organic matter, phytotoxicity). The aim of the present study was to evaluate the characteristics of a pharmaceutical sludge derived from the daptomycin production and to study the possibility of improving its quality through composting. The pharmaceutical sludge showed high content of macronutrients (e.g. total Kjeldahl N content was 38 g kg^{-1}), but it was also characterized by high salinity (7.9 dS m^{-1}), phytotoxicity (germination index was 36.7%) and a low organic matter stabilization. Two different mixtures were prepared (mixture A: 70% sludge + 30% wood chips w/w, mixture B: 45% sludge + 45% wood chips + 10% cereal straw w/w) and treated through static composting using two different aeration systems: active and passive aeration. The mixtures resulted in the production of two different compost, and the evolution of process management parameters was different. The low total solids and organic matter content of mixture A led to the failure of the process. The addition of cereal straw in mixture B resulted in increased porosity and C/N ratio and, consequently, in an optimal development of the composting process (e.g. the final organic matter loss was 54.1% and 63.1% for the passively and actively aerated treatment, respectively). Both passively and actively aerated composting of mixture B improved the quality of the pharmaceutical sludge, by increasing its organic matter stabilization and removing phytotoxicity.

1. Introduction

Sewage sludge are produced in wastewater treatment plants as the result of the total suspended solids removal and growth of microorganisms within biological treatments (Mailler et al., 2014). About 11 million tons of sludge (dry matter) are produced every year in Europe (EU-27) and their management is achieved through three main strategies: incineration, landfilling and agricultural reuse (Fytili and Zabaniotou, 2008). Council Directives (CEC, 2008, 1986) encourage sludge application to agricultural soils, due to their notable contents of organic matter and nutrients (Alvarenga et al., 2015). Agricultural reuse of sewage sludge faces social and technical obstacles (Cieślik et al., 2015), e.g. the sludge is produced during the whole year, whereas its application to the soils takes place once or twice a year. Furthermore, the benefits of sludge application to agricultural soils occur only if sewage sludge are applied according to good agricultural practices and climatic conditions (Alvarenga et al., 2015). Low organic matter stabilization and residual phytotoxicity are considered other limiting factors for the application of sewage sludge to agricultural soils (Oleszczuk, 2008). Recently, the presence in sewage sludge of emerging organic contaminants, such as pharmaceuticals, has been pointed out due to their possible transfer to the soil system through sludge agricultural reuse (Verlicchi and Zambello, 2015). Thus, the direct agricultural reuse of sewage sludge may be limited by the presence of pathogens, unstable organic matter and organic and inorganic pollutants.

Industrial fermentations for the production of a wide range of useful products (e.g. pharmaceuticals) generates large volumes of organic sludge that are usually disposed through incineration and landfilling (Fytili and Zabaniotou, 2008; Nithyanandam and Saravanane, 2013). In fact, their agricultural reuse is still limited, mainly due to the lack of evidences concerning their suitability for this purpose in terms of organic matter stabilization, phytotoxicity and macronutrients content. Composting is considered the best strategy to improve the quality of sludge (Alvarenga et al., 2015). During composting, the readily available organic components are

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degraded or transformed into stable humic-like compounds, enhancing the stability and maturity of the final compost (Said-Pullicino and Gigliotti, 2007; Said-Pullicino et al., 2007a,b). The high temperatures reached during the process (55–70 °C) and their maintenance during several days inactivate almost all pathogens (Cáceres et al., 2015; Czekala et al., 2016; Mc Carthy et al., 2011). In addition, a decrease of organic pollutants content and a reduction in the bioavailability of metal trace elements have also been reported during the composting of sewage sludge (Ho et al., 2013; Lau et al., 2003).

Although the agronomic value of pharmaceutical sludge may be improved through composting, a scarce literature concerning the aptitude of pharmaceutical sludge to be composted can be found (Majumdar et al., 2006). The occurrence of organic and inorganic contaminants (e.g. antibiotics, heavy metals), unbalanced C/N ratios and low total solids content in pharmaceutical sludge may result in the failure of their composting. Therefore, the control of process parameters is essential to ensure the correct behavior of composting process (Gigliotti et al., 2012; Hubbe et al., 2010; Jiang et al., 2011).

In this context, a pharmaceutical sludge obtained from the daptomycin production process was characterized and treated through different composting systems in order to obtain a high quality organic fertilizer. To achieve this aim, two different mixtures were treated through static composting and two different aeration systems (passively and actively aerated). In addition, several process parameters were monitored during composting.

2. Materials and methods

2.1. Organic materials origin and sampling

The pharmaceutical organic sludge studied in this work was originated from a daptomycin production plant (ACS Dobfar SpA, Anagni, Italy). Daptomycin is produced through the fermentation of a *Streptomyces roseosporus* biomass and, after the antibiotic separation, the residual wastewater is treated with a NaOH solution (to pH 12) to inactivate microorganisms and, then, it is processed in-situ in an aerobic wastewater treatment plant. The resulting sludge is immediately forced to pass through a belt press from which derives the pharmaceutical sludge (PS). A representative sample of the sludge was collected, cooled and stored at 4 °C for the transport to the laboratory. Once in the laboratory, the sample was divided in four aliquots: the first one was stored at 4 °C, the second one was frozen at −18 °C, the third one was oven-dried at 50 °C and the last one was freeze-dried.

For the composting experiment, bulking and absorbing agents (wood chips and cereal straw, particle size <50 mm) were collected from local farmers.

2.2. Pharmaceutical sludge characterization

Total solids (TS) and volatile solids (VS) content was determined according to standard methods (APHA, 2005). pH and electrical conductivity (EC) were measured in a solid/water suspension (1:10 w/v) by using a glass electrode (pH-Meter Basic 20+, Crison Instruments, Barcelona, Spain) and a conductivity probe (Ec-Meter Basic 30+, Crison Instruments, Barcelona, Spain), respectively. Total organic carbon (TOC) content was determined by the wet dichromate oxidation method (APHA, 2005). Fresh samples were used for the determination of total Kjeldahl-N and ammonium–N by means of macro and micro-Kjeldahl distillation methods, respectively (APHA, 2005). Total P was measured spectrophotometrically after digestion of the samples with concentrated H_2SO_4/$HClO_4$ (Gigliotti et al., 2012). Metals were extracted through digestion of the samples with HNO_3 and H_2O_2 by using a microwave oven (ETHOS One apparatus, maximum power 800 W, Milestone Inc., Bergamo, Italy). Total K and total Na were then determined through flame atomic emission spectroscopy, whereas heavy metals were determined through flame atomic absorption spectroscopy by using a Shimadzu AA-6800 apparatus (Shimadzu Corp., Tokyo, Japan). Total Hg was determined through a cold-vapour generator coupled to an atomic absorption spectrometer. *Escherichia coli* (*E. coli*) and *Salmonella* spp. were determined on fresh samples according to Standard Methods (APHA, 2005).

Analysis of daptomycin residues was carried out as briefly described below. Ten mg of freeze-dried sludge were extracted in 50 mL of $CH_3CN/NH_4H_2PO_4$ 0.45 M solution (80/20% v/v) for 24 h at room temperature on a mechanical shaker. The suspension was centrifuged at 12,000 rpm for 20 min and the supernatant was filtered on a membrane filter (0.45 μm). The obtained solution at different dilution rates (1:2, 1:5 and 1:20) was analyzed in a Perkin-Elmer PE 200 HPLC system, column IB-Sil C8-HC (5 mm × 250 mm × 4.6 mm Phenomenex) and pre-column IB-Sil C8 (5 mm × 30 mm × 4.6 mm Phenomenex). HPLC analysis were carried out with a flow of 1.8 mL min^{-1} of a mobile phase made of a $CH_3CN/NH_4H_2PO_4$ 0.45 M solution (80/20% v/v). The UV detector was set at 214 nm and the injection volume was 20 μL. The results were confirmed by using the standard addition method. Reference standard and system suitability standard of daptomycin were purchased by ACS Dobfar SpA.

The humic-like substances were extracted and purified as described by Ciavatta et al. (1990). C concentration in the fractions was determined by using a C analyzer (Multi N/C 2100 S analyzer, Analytik Jena, Jena, Germany). The degree of humification (DH) was also calculated as the percentage of the ratio (HA + FA)/TEC, where HA and FA represent humic and fulvic acids, respectively, whereas TEC is the total C extractable in alkali.

Water-extractable organic matter (WEOM) and its hydrophilic (Hi) and hydrophobic (Ho) fractions were obtained as described by Solé-Bundó et al. (2017) and Said-Pullicino et al. (2007a). C content in the fractions was then determined by using a C analyzer (Multi N/C 2100 S analyzer, Analytik Jena, Jena, Germany) and the Hi/Ho ratio was then calculated.

The determination of the germination index (GI) was conducted to assess the phytotoxicity of the sludge as described by Zucconi et al. (1985) and modified by Solé-Bundó et al. (2017) and Said-Pullicino et al. (2007a).

2.3. Composting experiment

2.3.1. Composting procedure

Bulking and absorbing agents (wood chips and cereal straw) were added to PS to modify the physical properties (bulk density, air-filled porosity and total solids) to avoid the leaching of free water and provide adequate air circulation. Based on these considerations, two mixtures were prepared according to the following proportions (fresh weight basis):

- Mixture A: sludge (70% w/w) and wood chips (30% w/w);
- Mixture B: sludge (45% w/w), cereal straw (10% w/w) and wood chips (45% w/w).

The main physico-chemical characteristics of both mixtures were determined and reported in Table 1. In particular, air-filled porosity was calculated from the wet bulk density as described by Alburquerque et al. (2008). The C/N ratios of both mixtures were not corrected since composting can be carried out effectively at low C/N ratios to reduce the requirement of bulking agent (Kumar et al., 2010).

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