HUMIC SUBSTANCES EXTRACTED FROM A BIO-STABILISED WASTE APPLYING DIFFERENT OPERATING CONDITIONS

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Humic substances are the major constituent of the organic matter of soil and sediments and are characterised by large amounts of functional groups (e.g. carboxylic and phenolic) that allow them to perform ionic exchange, complex formation and oxidation—reduction processes. For these characteristics these substances are used in different industrial applications, e.g. as textile detergents or surfactants. Nevertheless, these substances are also largely present in organic wastes and recently, applying a Circular Economy model, the research interest is focused on the possibility of extract these compounds from bio-stabilised wastes, such as compost (e.g. Montoneri *et al.,* 2009), Savarino *et al* (2010), Zingaretti *et al* (2018)). However, an interesting option could be to extract humic substances from other organic stabilised wastes that differently from compost has no further use. Hence, the aim of this study was to evaluate the possibility of extract Humic Substances (HS) from the bio-stabilised waste (BSW) produced from a Mechanical Biological Treatment (MBT) plant treating mixed residual solid waste, rather than the commonly used sources, as minerals or other carbon-rich matrices. Namely, the effects of the different operating conditions (i.e. material particle size, liquid-solid ratio, NaOH concentration and extraction time) applied for extracting humic acids were assessed.

The waste sample was collected from a MBT plant site near Rome. The humic acids were isolated by alkaline extraction adopting a modified version of the International Humic Substances Society method (IHSS 2018). Namely, the MBT waste sample was mixed with a NaOH solution at 65°C under N_2 gas atmosphere. Then, this slurry solution containing Soluble Bio-Organics substances was carefully separated from solid residues, mainly Humin (HU), by a 30min-centrifugation step at 4°C and 12000 rpm and by filtration on glass fiber membrane. The solution containing SBO was acidified with HCI to pH values lower than 2 in order to separate the fulvic acids (FA), that are water soluble complexes, from the humic acids (HA), that are insoluble for acidic conditions. After a precipitation step of about 3 h, a further centrifugation for 30min at 4°C and 12000rpm was performed so to enhance the HA separation yield. At the end of the extraction procedure, HA were air dried for 48 h before analysing their properties.

Five different extraction tests were performed on the bio-stabilised waste varying the material particle size (as received waste or d<0.5 mm), the liquid-solid ratio (10 or 5 L/kg), NaOH concentration (0.1 or 0.25 M) and the extraction time (4 or 24 h). Then, these tests were also repeated on the same bio-stabilised waste after a further maturation period in order to assess the effect of the matrix ripening on the extent of humic substances extraction. Namely, during this 180 days-maturation phase the bio-stabilised waste was manually overturned and water was added so to ensure the suitable conditions (aeration and moisture content) for the further biodegradation phase.

The main properties of the extracted humic acids were evaluated analysing the elemental composition (i.e. C, H, N, O and S content), the main functional groups (i.e. carboxylic and phenolic groups) by acid titration with HCI and the E4/E6 ratio by UV—VIS spectrophotometer (Chen *et al* 1977). As reference, the same analyses were performed on a sample of the commercial humic acids purchased by Sigma—Aldrich.

The further maturation period applied on the bio-stabilised waste proved to significantly improve the amount of extracted humic acids that passed from 0.4-25 g HA/kg BSW to 21-60 g HA/kg BSW for BSW that underwent at least 90 days of further maturation (Figure 1a). Similarly also the amount of fulvic acids extracted from the bio-stabilised waste was favorably influenced by the applied maturation period (Figure 1b). Comparing the properties of the different humic acids extracted from the bio-stabilised waste before the ripening period, the operating conditions that showed to improve the extraction extent were the NaOH concentration and the extraction time. The HA obtained in these specific conditions showed higher functional group content and aromaticity compared with the substances extracted at the others operating conditions. The substances isolated from the MBT waste after a 180 days-maturation phase, instead, showed only slight differences due to the specific operating conditions applied, suggesting that after the maturation stage also milder operating conditions allow to extract humic acids with similar chemical properties.

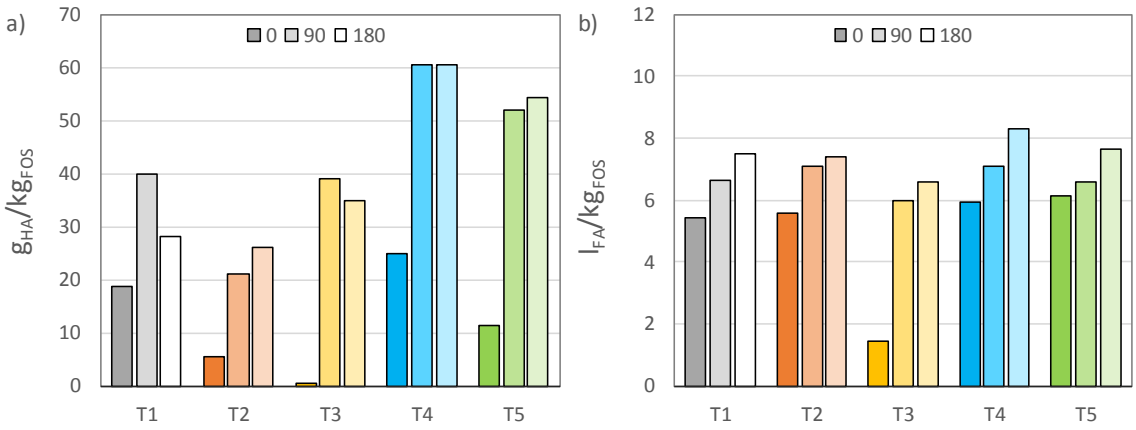

Figure 1. Amount of the extracted humic substances: a) Humic Acids; b) Fulvic acids

These results were also confirmed by the spectrophotometric analysis that showed higher differences for E4/E6 ratio with the specific operating conditions applied for the bio-stabilised waste before maturation compared with the one obtained after 180 days, that resulted more than twice. Besides, the humification index (HI) of the extracted substances, that as defined by Bustamante *et al* (2012) represent the ratio between the carbon content of humic acids and the total carbon content of the matrix, prove to significantly increase. The obtained results showed that the extraction of humic acids from MBT waste could be an interesting option since the isolated substances present chemical properties comparable with those observed in the commercial HA or in the ones extracted from compost.

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