The Most Appropriate Way to Increase the Quality Indices of the Humic Acid Extracted from Vermicompost

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Abstract Vermicompost is a plant growth-promoting biofertilizer that has a large amount of humic acid (HA). Use of humic acid in the world, as soil amendments or for enhancing the performance of the products in order to achieve sustainable agriculture, is constantly increasing. In the present study, various methods to increase the efficiency of extracted humic acid from vermicompost were assessed. Humic acid extraction was conducted using alkaline methods at various extraction times with two extractants including urea (0.5 M) and NaOH (0.5 M). Elemental composition, functional group content and spectrophotometric ratios were measured. Results showed that humic acid extracted with urea has lower C/N and ash and more functional groups and higher spectrophotometric ratios than humic acid extracted with NaOH. In addition, the nature of the extracted humic acid was destroyed with increasing the extraction time. Finally, to increase the efficiency of extracted humic acid, the use of urea as an extractant for 1 day is proposed as an appropriate method.

Keywords Extractants • Functional groups • Humic acid • Vermicompost

Introduction

The isolation of humic acid (HA) from soil and/or different organic raw matter always has been a challenging task for researchers. However, basic extractant solutions may produce humic substances (HS), and thus, HA oxidation, hydrolysis and cleavage reactions are possible. These kinds of transformations may be different according to the source of HA, the isolation conditions and variations in the

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extraction time. The different solubility of HS in the different extractants can result from the differences in the chemical structure of the macromolecules or the physical protection of the organic macromolecules complexed with the minerals fraction through the cation bridges. Extraction with NaOH extractants can produce relatively high yields of organic matter, but the extraction has to be repeated several times to achieve maximum recovery (Stevenson 1994).

With respect to extraction time, the different extraction methods have several variations in which the soil or organic raw material samples remain in the extractant solution, e.g. from 4 to 24 or to 48 h (Prentice and Webb 2010).

The differences in the soil HA macromolecules regarding their solubility, composition, structure and chemical characteristics depend on the isolation procedure, i.e. repetitive isolation, time of isolation and kind of extractant solution. High alkaline extraction media and successive extraction could change the macromolecular structure of the humic acid, resulting in aggregation, disaggregation, recombination or other chemical processes that form new compounds during the isolation procedure (Stevenson 1994). Because of the chemical nature of humic acid, successive extraction of humic acid fractions with NaOH solution could lead to important structural differences from the former to last humic acid isolation, even, from the same soil sample. As the time of contact of the HA with the isolation solution increases, the structural changes in the macromolecule could be more pronounced.

The aim of this study was evaluation of the most appropriate way to increase the quality of the extracted humic acid from vermicompost as a plant growth-promoting biofertilizer.

Materials and Methods

The organic material used for humic acid isolation was vermicompost obtained from cow manure and crop residues in a ratio of 1:1. The HA was extracted with 0.5 mol L^{-1} NaOH and urea to stand at different times (1, 7 or 9 days) as described in Qi et al. (2004). Extraction of humic acid was conducted in five replications, and data were presented.

The elemental compositions were determined by an Elementar Analysen System GmbH Vario EL. Total acidity, carboxylic groups (COOH) and total hydroxyl content were determined according to conventional methods described by Page (1982), and phenolic-OH group content was calculated by difference.

E_3/E_5 and E_4/E_6 ratios were determined according to conventional methods described by Campitelli et al. (2006) and Abbt-Braun and Frimmel (1999). All of the analyses were carried out in three replication for each trait.

Results and Discussion

The humic acid isolated with urea (HA-urea) has higher N content than the humic acid isolated with NaOH 0.5 mol L^{-1} (HA-NaOH), probably, due to the nitrogen in the extractant solution. In general, there was a decrease in C/N ratio with increasing saturation with N (urea) (Table 1).

The H/C ratio represents the degree of the HA unsaturation. This ratio for HA-urea is higher than that obtained for HA-NaOH, indicating that HA-urea has a great degree of saturation, probably due to the different acid–base characteristics of the urea solution, or the different kind of reactions that can take place with the macromolecules.

The acidic functional group content (total acidity, carboxylic and phenolic-OH groups) of the HA-urea, specifically the phenolic-OH, was higher than that corresponding to the HA-NaOH. This result is in agreement with the higher H content for HA-urea and the probably disaggregation produced by the urea solution (Table 2).

In this study, the acidic groups decreased with increasing extraction time, and hydroxyl groups increased. With increasing extraction time, changes in the nature of humic acid were observed because of the heterogeneous molecular structure and chemical nature of humic acid. Humic acid that was extracted with NaOH and urea solutions can show significant structural differences, even, if they are extracted from the same vermicompost (Table 2).

The E_4/E_6 ratio is related to the degree of condensation of the aromatic C network, and the E_3/E_5 ratio changes inversely with the mean molecular size.

HA-urea has a high value of both ratios (Table 3), indicating a higher content of aliphatic chains or a greater disaggregation than HA-NaOH. HA-urea also has a smaller molecular size, in agreement with the data about acid groups, in particular phenolic groups (Table 3).

Table 1 Elemental composition (ash and moisture-free basis), H/C and C/N ratio of the studied HA

HA sample	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)	H/C	C/N
HA-NaOH 0.5 mol L^{-1}	54.8	3.9	3.7	0.5	37.1	2.6	0.91	9.25
HA-urea 0.5 mol L^{-1}	53.1	4.9	5.1	0.4	36.5	1.7	1.12	6.41

Table 2 Acidic functional groups contents of the studied HA (mmol g^{-1})

	Total acidity			Carboxylic groups			Phenolic-OH group			Total hydroxyls		
HA sample	1[a]	7[a]	9[a]	1[a]	7[a]	9[a]	1[a]	7[a]	9[a]	1[a]	7[a]	9[a]
NaOH[b]	5.7	5.55	5.20	3.01	2.96	2.91	2.69	2.59	2.29	2.90	3.50	3.75
Urea[c]	7.63	7.25	7.01	3.89	3.66	3.61	3.74	3.59	3.39	2.90	3.50	3.70

[a] Extraction time
[b] HA-NaOH 0.5 mol L^{-1}
[c] HA-urea 0.5 mol L^{-1}

Table 3 The absorbance ratios at particular wavelengths (E_3/E_5; E_4/E_6) for HAs extracted from vermicompost

	E_3/E_5			E_4/E_6		
HA sample	1^a	7^a	9^a	1^a	7^a	9^a
NaOH[b]	5.51	5.17	5.10	4.51	3.83	3.72
Urea[c]	5.45	5.38	5.21	5.19	5.08	4.86

[a] Extraction time
[b] HA-NaOH 0.5 mol L^{-1}
[c] HA-urea 0.5 mol L^{-1}

As shown in Table 3, with increasing extraction time, generally optical absorption, E_3/E_5 and E_4/E_6 ratios decrease, and with the increasing extraction time, the nature of humic acid changes. In fact, with increasing extraction time, the macromolecular structure of the humic acid could change, suffering aggregation, disaggregation, recombination or other different chemical process to form new compounds during the isolation procedure (Stevenson 1994).

Conclusions

The different types of extractant solutions and extraction time have significant effects on extracted humic acid properties. Increasing the extraction time has a destructive effect on extracted humic acid. The quality of humic acid extracted with urea is better and has positive features such as higher functional groups, lower C/N ratio and high ratios of H/C, E_4/E_6 and E_3/E_5.

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