

ALKALINE EXTRACTION OF HUMIC SUBSTANCES FROM PEAT APPLIED TO ORGANIC-MINERAL FERTILIZER PRODUCTION

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Abstract - An organic-mineral fertilizer based on humic substances (HSs) and potassium was developed based on the alkaline extraction of HSs from peat. The HSs have interesting properties for use as a fertilizer since they improve the physical and chemical structure of the soil and provide a source of organic carbon which is readily absorbable by the plants, whereas potassium is a primary nutrient for plants. It was found that highly decomposed peats containing a small inorganic fraction are more favorable for the extraction of HSs. Using these peats, organic-mineral fertilizers that meet the Brazilian legislation have been obtained for a peat-extractant mixture containing 2.57 wt% total organic content (TOC), a K₂O/TOC ratio of 1 wt% and an extraction time of 12 hours.

Keywords: Peat; Humic substance; Humic acid; Fertilizer; Organic-mineral fertilizer; Alkaline extraction.

INTRODUCTION

Organic matter applied to the soil favors the development and growth of plants because it supplies macro- and micronutrients, reduces soil toxicity through heavy metal complexation (Brown *et al.*, 2000), improves the physical and chemical characteristics of the soil and prevents nutrient loss by leaching (Kiehl, 1985; Stevenson, 1994). Organic fertilization of soil reduces or even precludes the need for agrochemicals and mineral fertilizers (Penteado, 2000), the extensive use of which results in economic and environmental imbalances. Whenever possible, organic fertilization relies on the use of manure,

culture alternation, green fertilization, composting and biological control of pests and diseases. With its 1.77 million hectares of land area certified for organic agriculture, Brazil occupies the world's third position. With regard to land for extractivism, its 6.18 million hectares place this country in the 2nd place (IFOAM, 2012). Fifteen thousand certified properties, 70% of which represent family agriculture, respond for 3.8% of the world consumption of organic agriculture, a consumption that grows 30% yearly. The use of organic matter in agriculture is also widespread in Asia and Europe (Santos Jr., 2003).

About 80 to 90 wt% of the organic matter found in the earth's crust is constituted of humic substances

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(HSs) (Aiken *et al.*, 1985). HSs play important roles in plant development. They reduce the hydric stress in plants (Altiere, 1999). Due to their dark color, they contribute to heat retention in the soil which is beneficial for seed germination. Besides, they interact with the cellular metabolism of plants, facilitating the absorption of nutrients and enzymatic activity (Pimenta *et al.*, 2009; Varazini *et al.*, 1993). They change the physical structure of the soil, stimulate microbial activity and promote the solubilization of complexes (Silva, 2001). Numerous studies have shown the beneficial effects of HSs on specific crops, such as barley (AYUSO *et al.*, 1996), olive trees (Fernandez-Escobar *et al.*, 1996; Murillo *et al.*, 2005), corn (Eyheraguibel *et al.*, 2004; Andrade *et al.*, 2004), oats (Rosa *et al.*, 2004), grapes (Basso *et al.*, 2005) and cocoa trees (Calima *et al.*, 2005). The effects of HSs on the growth of numerous species have been reviewed by Chen and Aviad (1990).

Much of the HSs used in organic fertilizers is derived from leonardite, a material with a HSs content of over 90 wt%. In Brazil leonardite deposits are not found, so one has to consider other sources of HSs, such as mineral coal, lignite, worm compost and peat. Mineral coal is not an attractive source because it contains less than 10 wt% in HSs (Clasen *et al.*, 1998). Lignite recovery is not economical. Worm composts contain up to 80 wt% of HSs, but are cumbersome and expensive for large scale production (Castilhos *et al.*, 2008). An attractive alternative is peat, which contains HSs in acceptable concentrations, varying between 20 and 40 wt%, and is simple to recover either from surface deposits or as a by-product in sand mining (Davis, 1985).

Peat is an organic-mineral fossil found in swampy areas, flood plains, plain coastal areas and lakes (Spedding, 1988; Davies, 1985; Fuchsman, 1980). It is formed by the deposition of layers of sand, silt, clay and plant matter, which undergo microbiological and chemical transformations on a timescale of hundreds of years (Stach *et al.*, 1975). The resulting organic material is mainly originated from the chemically more stable compounds of the original plant tissues, such as lignin, cellulose and hemicelluloses, whereas the water soluble compounds such as simple sugars and amino acids are hardly present in peat (Fuchsman, 1980). The organic matter found in peat can be classified as humified, partly humified and raw organic matter (Franchi, 2000). The HSs in peat are a complex mixture of molecules of low molecular weight (Tsutsuki and Kuwatsuka, 1978) and high stability in comparison with non-humic substances. HSs are constituted of humic acids, fulvic acids and humins. Besides HSs, peat also contains

resinous materials, carbohydrates related to cellulose fibers, lignin and inorganic matter, such as salts, sand, silt and clay. Peat can be classified in the following types (International Peat Society, 2013): (i) light peat, which is little decomposed, generally reddish brown, with the organic portion containing more than 2/3 of vegetable fibers; (ii) dark peat, which is intermediately decomposed, with a fiber content of 1/3 to 2/3 of the organic matter; (iii) black peat, highly decomposed and having 1/3 of the organic matter as fibers.

HSs from peat may be processed into organic-mineral fertilizers that may be applied in the soil, in fertirrigation or as foliar fertilizers to provide the benefits of organic fertilizers, as well as the mineral macronutrients needed for plant nutrition (Adriese, 1988; Kiehl, 1985). Organic-mineral fertilizers are particularly effective because they provide slow released nutrients and reduce nutrient leaching due to mineral adsorption and complexation with HSs (Kiehl, 1985).

In this work a process is proposed for production of a fluid organic-mineral fertilizer from peat and potassium hydroxide. The latter compound simultaneously serves as an extractant for the HSs in peat and as a macronutrient for plant growth. So far, much is known about the alkaline extraction of HSs from peat, but this process has been studied mostly from an analytical perspective, so that conditions suitable for fertilizer production are not known. Therefore, this contribution is focused on finding the conditions that maximize the recovery of HSs from peat and that minimize the consumption of KOH while obeying the Brazilian legislation (MAPA, 2009) for fluid organic-mineral fertilizers, which specifies minimum mass fractions in the product for the total organic carbon and for the sum of macronutrients (N, P₂O₅ e K₂O) as 3 wt% each.

EXTRACTION OF HUMIC SUBSTANCES FROM PEAT

The classical procedure for HSs recovery from organic matter consists of an alkaline extraction of humic and fulvic acids, leaving a solid residue formed by humin and inorganic matter. Acidification of the alkaline extract promotes the precipitation of the humic acids, leaving fulvic acids in solution (Benites *et al.*, 2003). This procedure leads to the separation of organic matter into fractions that are mixtures of compounds with similar chemical characteristics (MacBride, 1994).

Extractants containing hydroxides and sodium

carbonates in concentrations of 0.1 N and 0.5 N are effective for removal of HSs from soil if used sequentially (Rosa, 1998; Rosa *et al.*, 1999). Separation of HSs from peat with a grain size below 0.21 mm was found to be optimal by using as extractant a 0.5 N KOH solution, an extraction time of 4 h and a peat-to-extractant ratio of 1:20 (mass:volume) at 25 to 30 °C under a nitrogen atmosphere with mechanical agitation. It was also found that a larger amount of HSs of higher purity was obtained with KOH in comparison with NaOH. The method was effective in separating the HSs from peat, but delivered a diluted extract.

Although effective, alkaline extractants may partially hydrolyze or self-oxidize the organic matter (Stevenson, 1994; Rosa *et al.*, 1998). Extraction times of several hours are necessary because of the slow depolymerization of complexes of high molecular weight (Stevenson, 1994). It has been observed in aerated solutions of pH values above 8 that the extraction is accompanied by substantial oxygen consumption.

Alkaline treatment also causes an undesirable contamination of the extracted HSs with co-extracted substances, such as silica, salts, clay, protoplasmatic and structural components of fresh organic tissues (Stevenson, 1994). High temperatures should be avoided as they promote the degradation of amino acids present in the molecular chains of humic acids (Yamamoto *et al.*, 1994).

METHODS

Peats from four locations in Brazil were selected to represent a wide range of degree of decomposition. They were Fraga Rizzo peat, Darci peat, both from the region of Cravinhos, São Paulo; Florestal peat and Kurt peat from the city of Criciúma, Santa Catarina. Peat samples were obtained directly from peat producers in shipment/cargos. The *in natura* samples were not modified by any chemicals or additives. The collected peat was disc milled (Marconi, model MA 630/1), sieved for selection of particles smaller than 0.1 mm and homogenized for ten minutes in a Y mixer. The extractants were aqueous solutions of KOH prepared with analytical grade KOH and deionized water. The extractions were conducted in a 0.4L beaker with a diameter of 0.09 m and a height of 0.097 m provided with a four-blade 45° pitched blade stirrer having a diameter of 0.04 m. The rotation speed was 300 r.p.m. No provision was taken to avoid the contact of the suspension with atmospheric air.

Exploratory extraction experiments consisted of

mixing 20 g of dry peat with 100 mL of KOH solutions of concentrations of 0.5, 1.0, 1.5 or 2.0 M during 12 and 24 h. After extraction, the solution containing HSs was separated from the insoluble fraction containing humin by centrifugation at 2500 r.p.m. for 10 minutes. The experiments were performed in triplicate. All extraction experiments were conducted at room temperature (25 ± 2 °C). Details of the experimental methods are found in Saito (2012).

Additional experiments were performed in which the contents of both TOC and K₂O in the peat-extractant mixture were varied, expressed as the quantities TOC_{FEED} and K₂O/TOC_{FEED}, where the subscript “feed” refers to the peat-extractant mixture. The TOC_{FEED} values varied from 0.86 to 6.17 wt% and the K₂O/TOC_{FEED} varied from 0.6 to 1.4 wt%. The extraction time was 24 h.

Finally, experiments were performed in an attempt to reduce the extraction times to 3, 6 and 12 h. In these experiments the TOC_{FEED} was varied within the range of 2 to 4 wt% and the K₂O/TOC_{FEED} assumed the value of 1 wt%. Other conditions were as described before.

The peat and the extract were characterized with respect to the organic matter content, the total organic carbon (Ciavatta method) and the HSs content (humic and fulvic acids separately) using the method suggested by the IHSS, International Humic Substances Society. Electrical conductivity of peat was measured as an indication to the amount of salts. Visual and tactile observation of the peat was used for qualitative assessment of the collective presence of clay, silt and sand, as well as of the fiber content.

RESULTS

Peat Characterization

The organic fraction of peat is expressed either as the dry organic matter or as the total carbon content and its degree of decomposition is proportional to the content in humic and fulvic acids (Stevenson, 1994). A low degree of decomposition is also visually assessed by a high fiber content. The inorganic content is inferred from the total carbon content (being low as the total carbon content is high), as well as from visual observation. The nature of the inorganic fraction is inferred from the electrical conductivity: a high conductivity indicates the substantial presence of salts, whereas a low value indicates that neutral molecules such as sand, silt or clay are present. The presence of these neutral compounds collectively is also visually observed.

Tables 1 and 2 give the relevant physical and chemical characteristics of peats from the four different locations. The Fraga Rizzo and Darci peats have low organic contents and high degrees of decomposition in comparison to the Florestal and Kurt peats; therefore, their organic carbon are predominantly present in the form of HSs (for the Darci peat the sum of HA and FA even matches OM_{DB} within experimental error, indicating that all of the organic matter is decomposed). These ideas are consistent with the visual observation of lower amounts of undecomposed fibers in the former two peats in relation to the latter two ones.

The Darci peat has the lowest organic carbon content of all four peats; therefore it is the highest in inorganic fraction. Since the electrical conductivity is low, its salt content is low and its content in neutral inorganic molecules such as clay, silt and sand is high. Excessive clay in peat may negatively affect the amount of humic extract recovered by centrifugation during the industrial processing of peat.

The Kurt peat is more decomposed than the Florestal peat, as evidenced by the higher contents in humic and fulvic acids, as well as the less significant presence of decomposed fibers. The Kurt peat con-

tains less dissolved salts (inferred from its lower electrical conductivity) and less inorganics (deduced from its higher TOC) than the Florestal peat. Inorganics are potentially harmful to industrial centrifuges due to the abrasive nature of their sand fraction.

Table 3 summarizes the main characteristics of the four peats in relation to their quality as a raw material for the proposed organic-mineral fertilizer. The Fraga Rizzo and Kurt peats are probably suitable raw materials, given the high degree of decomposition and low amount of clay and sand.

Exploratory Extraction Experiments

Extraction experiments in which the peat-to-extractant mass ratio was fixed were considered first. Figure 1 shows that the total organic content in the extract (TOC_{EX}) is generally higher for an extraction period of 12 h than for 24 h. This result is explained by the aeration promoted by agitation, which promoted oxidation of organic matter. Indeed, additional measurements (not shown) revealed that the organic content of both the extract and the solid residue decreased for extraction times from 12 h to 24 h.

Table 1: Moisture content, density, pH and electrical conductivity of peat from different locations. Mean values of determinations in triplicate are given.

Peat location	Moisture content wt%	Density $kg.L^{-1}$	pH	Electrical conductivity $mS.cm^{-1}$
Fraga Rizzo	30.33	708.4	4.95	0.10
Darci	17.32	851.4	4.76	0.09
Florestal	32.11	545.5	6.36	0.23
Kurt	54.24	757.5	4.98	0.02

Table 2: Organic matter, total organic content, humic acid and fulvic acid contents in peats from different locations in weight percent dry basis.

Peat location	OM_{DB} (wt%)	TOC_{DB} (wt%)	HA (wt%)	FA (wt%)
Fraga Rizzo	41.35	19.70	35.50	1.37
Darci	29.98	14.52	28.10	2.68
Florestal	67.55	29.12	25.30	1.74
Kurt	68.14	38.79	29.77	2.85

Table 3: Main characteristics of peat from different locations. The rightmost column indicates the peat quality as a raw material for the proposed organic-mineral fertilizer.

Peat	Organic content	HSs content	Neutral inorganics content	Salt content	Quality
Fraga Rizzo	++	+++	+	+	High
Darci	+	++	+++	+	Low
Florestal	+++	+	++	++	Médium
Kurt	+++	++	++	+	High

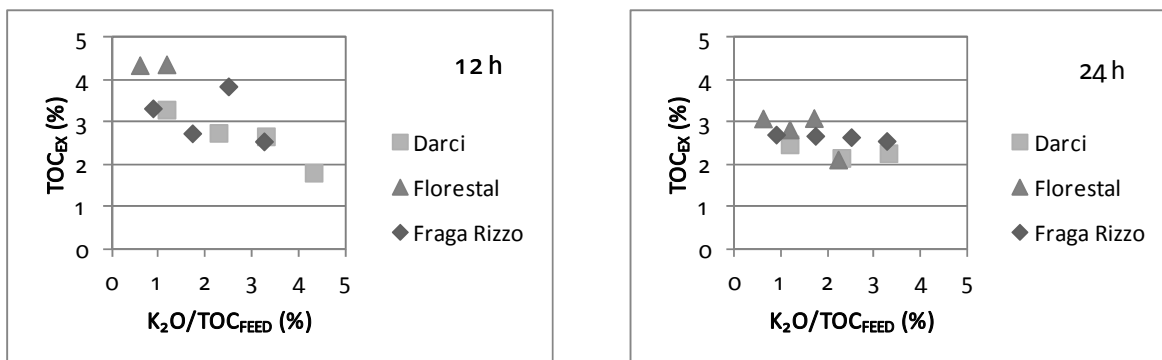


Figure 1: Total organic content in the extract from exploratory experiments after extraction times of 12 h (left) and 24 h (right).

Figure 1 also shows that the TOC_{EX} is higher for lower KOH concentration, expressed as the feed ratio K₂O/TOC_{FEED}. It is likely that the higher extraction rates are due to a faster diffusion coefficient for humic acids, which in turn are associated with a favorable conformation of the humic acid molecules in solution at lower pH and ionic strength values (Wang *et al.*, 2001).

Figure 2 shows that the TOC_{EX} is higher when TOC_{FEED} is higher, that is, more HSs are extracted when the peat is richer in organic matter.

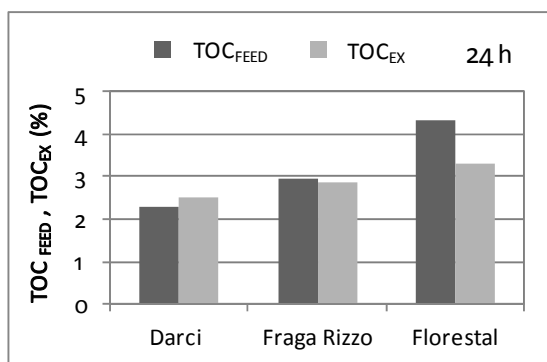


Figure 2: Total organic carbon in the extraction mixture and in the extract for different peats.

From this perspective, a peat with a higher total organic carbon such as the Florestal peat should be preferred. However, for this peat the amount of TOC extracted per unit TOC_{FEED} is less than with the other peats, because it has the lowest degree of decomposition and the highest salt content of all three peats (see Table 3). Therefore, both a high total organic content and a high degree of decomposition are

desirable characteristics. In this comparison, the Fraga Rizzo peat is the most suitable raw material of the three as it delivers an extract within the commercial specification (a TOC_{EX} of 3 wt%), provided that the K₂O/TOC ratio is 1.5 or lower and the extraction time is 12h.

Choice of the Peat-to-Extractant Ratio

Extraction experiments are next considered in which the amounts of peat and extractant varied. Figure 3 shows that, as expected, the organics content in the extract (TOC_{EX}) increases with the amount of peat used (here expressed as the TOC content in the extraction mixture TOC_{FEED}). However, the amount of extracted TOC does not increase proportionally to the amount of peat. In order to evaluate this aspect quantitatively, the extraction efficiency is considered, which is defined as the ratio of the amount of total organic carbon in the extract to the amount of total organic carbon in the peat. Figure 4 shows that the efficiency is within the range of 65 to 98%, the highest values occurring when little peat is added, i.e., for lower values of TOC_{FEED}. Figures 3 and 4 also show that both the extracted carbon TOC_{EX} and the efficiency are inversely related to the K₂O/TOC_{FEED} ratio. These results hold true irrespective of the peat source.

From the above, as the TOC_{FEED} increases, the concentration of TOC in the extract increases, but the efficiency decreases. Therefore, in order to obtain a TOC_{EX} of 3 wt% or more to meet the organic-mineral fertilizer specification, as well as a high extraction efficiency of 90 wt% or more, a TOC_{FEED} of 2.57 wt% and a K₂O/TOC_{FEED} mass ratio of 1 would be suitable choices for both the Darci and the Kurt peats.

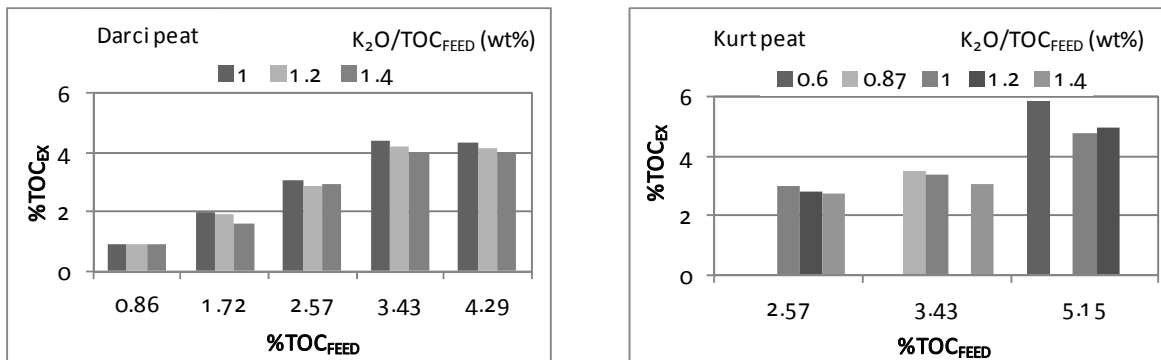


Figure 3: Total organic content in the extraction mixture (TOC_{EX}) for varying amounts of peat (expressed as TOC_{FEED}) and alkali additions (expressed as the K₂O/TOC_{FEED}). Darci (left) and Kurt peat (right). The extraction lasted 24 h.

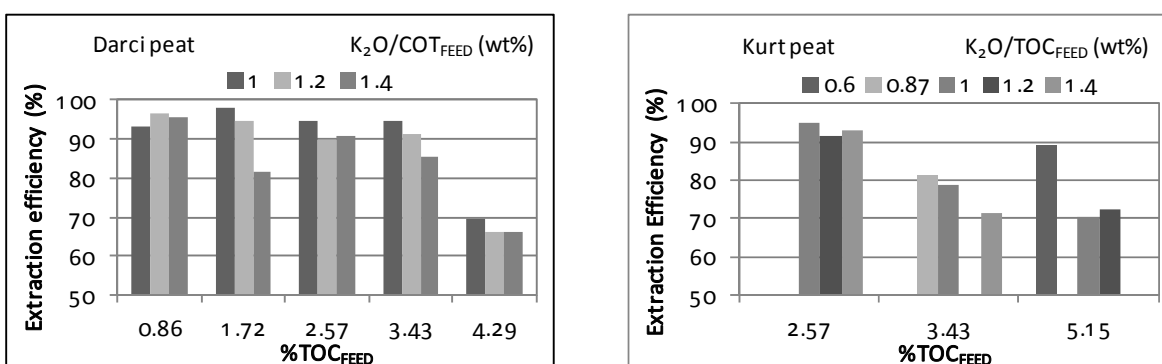


Figure 4: Peat extraction efficiency (total organic carbon extracted per unit total organic carbon in the peat) for varying amounts of peat (expressed as TOC_{FEED}) and alkali additions (expressed as the K₂O/TOC_{FEED}). Darci (left) and Kurt peat (right).

Choice of the Extraction Time

Since extraction periods of 12h were more effective than 24 h, further experiments were performed with shorter periods of time. Figure 5 shows that, independent of the peat source, extraction times smaller than 12 h lead to lower concentrations of TOC in the extract (TOC_{EX}) and to lower extraction efficiencies.

Therefore, an extraction time of 12 h appears to be the best value among the investigated values, irrespective of the peat source. It is concluded that this period of time is necessary to break the bonds between the inorganic components and the organic matter of peat, as well as to depolymerize high molecular weight complexes, thereby solubilizing the HSs. Longer periods of time favor the oxidation of the HSs.

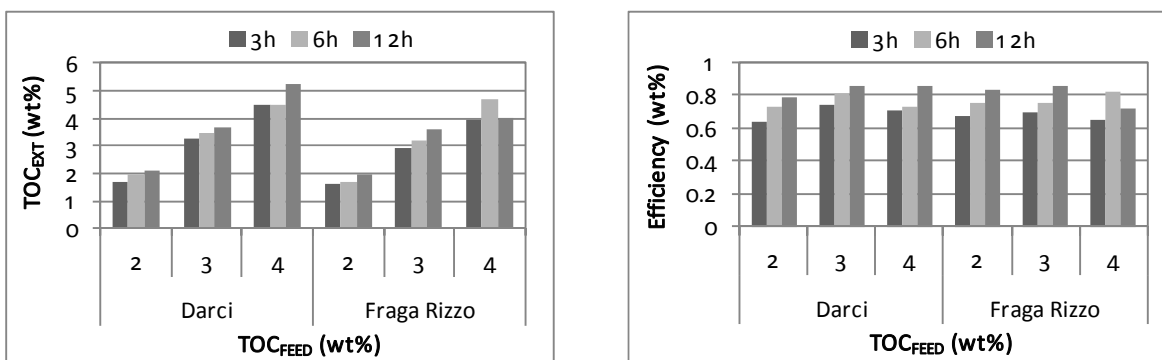


Figure 5: Total organic content in the extraction mixture (TOC_{EX}) (top) and extraction efficiencies (bottom) for shorter extraction times and TOC_{FEED} values of 2, 3 and 4 wt%.

CONCLUSIONS

A process was developed for the production of an organic-mineral fertilizer containing HSs and potassium. The process is based on the alkaline extraction of HSs from peat. Peats suitable for organic-mineral fertilizer production should be rich in organic matter and well decomposed in order to provide a high HSs content in the extract and a high extraction efficiency. They should also contain little fiber and inorganic components such as sand and clay, which negatively interfere with the separation of the solid residue. The extraction efficiency was found to be inversely related to the amount of alkali added. A low value of 1 is suggested for the mass ratio of the potassium extractant to the total organic carbon in the extraction mixture (K_2O/TOC_{FEED}). The peat-to-extractant ratio is directly related to the extractant TOC and inversely related to the TOC extraction efficiency. Therefore, in order to obtain both an organic carbon content in the extract (TOC_{EX}) of at least 3 wt%, which meets the organic-mineral fertilizer specification, and a high extraction efficiency of 90 wt% or more, the peat-to extractant ratio that corresponds to a total organic content in the extraction mixture (TOC_{FEED}) of 2.57 wt% would be a suitable choice. The extraction efficiency was found to increase with time up to 12 h and to decrease thereafter due to the oxidation of the organic fraction.

SYMBOLS

FA	Fulvic acid
HA	Humic acid
HSs	Humic substances
K_2O	Potassium oxide
OM	Organic matter
TOC	Total organic carbon

Subscripts

DB	dry basis
EX	extract, i.e., soluble fraction of the peat-extractant mixture after extraction
FEED	peat-extractant mixture fed to the extractor

REFERENCES

- Adriessse, J., Nature and management of tropical peat soils. FAO Soils Bulletin 59. FAO, Food and Agricultural Organization of the United Nations, Rome (1988).
- Aiken, G. R., McKnight, D. M., Wershaw, R. L. and MacCarthy, P., Humic Substances in Soil, Sediment and Water: Geochemistry, Isolation and Characterization. Wiley, New York (1985).
- Altiere, M. A., The ecological role of biodiversity in ecosystems. *Agriculture, Ecosystems and Environment*, Charlottetown, 74(1-3), p. 19-31 (1999).
- Andrade, F. V., Mendonça, E. S., Silva, I. R. and Mateus, R. F., Low molecular weight and humic acids increase phosphorus uptake and corn growth in Oxisols. In: Humic substances and soil and water environment, Embrapa Instrumentação, São Pedro, p. 211-214 (2004).
- Ayuso, M., Hernández, T., Garcia C. and Pascual, J. A., Stimulation of barley growth and nutrient absorption by humic substances originating from various organic materials. *Bioresource and Technology*, 57(3), p. 251-257 (1996).
- Bassoi, L. H., Silva, S. T. and Silva Filho, A. V., Efeito da aplicação de ácidos orgânicos na produção de uva cv. Itália no Vale do São Francisco. In: Encontro Brasileiro de Substâncias Húmicas, 6: Embrapa Solos, p. 1-3, Rio de Janeiro (2005). (In Portuguese).
- Benites, V. M., Madari, B. and Machado, P. L. O. A., Extração e fracionamento quantitativo de substâncias húmicas do solo: Um procedimento simplificado de baixo custo. Embrapa Solos. Comunicado Técnico, 16, p. 7, Rio de Janeiro (2003). (In Portuguese).
- Brown, P. A., Gill, S. A. and Allen, S. J., Metal removal from wastewater using peat. *Water Research*, 34, p. 3907-3916 (2000).
- Calima, D. F., Paneto, R. O., Aguilar, M. A. G., Folli, F. B., Souza, C. A. S. and Sonegheti, S., Crescimento e fotossíntese de clones de cacau (*Theobroma cacao* L.) com resistência diferencial a *Verticillium dahliae* submetidos diferentes doses de Turfa Líquida®. In: Encontro Brasileiro de Substâncias Húmicas, 6, Embrapa Solos, p. 9-11, Rio de Janeiro (2005). (In Portuguese).
- Castilhos, R. M. V., Dick, D. P., Castilhos, D. D., Morselli, T. B. A. G., da Costa, P. F. P., Casagrande, W. B. and Rosa, C. M. C., Distribuição e caracterização de substâncias húmicas em vermicompostos de origem animal e vegetal. *R. Bras. Ci. Solo*, 32, p. 2669-2675 (2008). (In Portuguese).
- Chen, Y. and Aviad, T., Effects of humic substances on plant growth. In: MacCarthy, P., Clapp, E. E., Malcolm, R. L., Bloom, P. R. (Eds.) Humic Substances in Soil and Crop Sciences: Selected Readings, American Society of Agronomy, Madison (1990).
- Clasen, H. A. C., Lessa, R., Kaemmerer, M. and Koetz, P., Ácidos húmicos e fúlvicos do carvão em jazida de candiota. *Rev. Bras. de Agrociência*, 4(1), p. 35-40 (1998). (In Portuguese).
- Davis, C. L., Peat. In: Mineral Facts and Problems.

- US Bureau of Mines/DBI. Washington DC, p. 563-568 (1985).
- Eyheraguibel, B., Silvestre, J. and Morard, P., Physiological effects of humic like substances on maize. In: Humic Substances and Soil and Water Environment: Embrapa Instrumentação, São Pedro, p. 200-202 (2004).
- Fernández-Escobar, R., Benloch, M., Barranco, D., Dueñas, A. and Gutiérrez Gañán, J. A., Response of olive trees to foliar application of humic substances extracted from leonardite. *Scientia Horticulturae*, Amsterdam, 66(3-4), p. 191-200 (1996).
- Franchi, J. G., Aplicação de turfa na recuperação de solos degradados pela mineração de areia. *Boletim Técnico da Escola Politécnica da USP, Departamento de Engenharia de Minas*, São Paulo (2000). (In Portuguese).
- Fuchsman, C. H., Peat - Industrial Chemistry and Technology. Academic Press, New York (1980).
- IFOAM, The world of organic agriculture- Statistics and emerging trends, FiBL – Research Institute for Organic Agriculture and IFOAM – International Federation of Organic Agriculture Movements (2012).
- IPS, International Peat Society, Jyväskylä, Finland, <http://www.peatsociety.org/> (2013).
- Kiehl, E. J., Fertilizantes Orgânicos. *Agronômica Ceres*, São Paulo (1985). (In Portuguese).
- MAPA, Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa No. 25, 23 de junho (2009). (In Portuguese).
- McBride, M. B., Environmental Chemistry of Soils. Oxford University Press, New York (1994).
- Murillo, J. M., Madejón, E., Madejón, P. and Cabrera, F., The response of wild olive to the addition of a fulvic-rich acid amendment to soils polluted by trace elements. *Journal of Arid Environments*, London, 63, p. 284-303 (2005).
- Penteado, S. R., Introdução à Agricultura Orgânica – Normas e Técnicas de Cultivo. Editora Grafimagem, Campinas (2000).
- Pimenta, A. S., Santana, J. A. S., dos Anjos, R. M., Benites, V. M. and Araújo, S. O., Caracterização de ácidos húmicos produzidos a partir de carvão vegetal de duas espécies florestais do semi-árido: Jurema preta (*Mimosa tenuiflora*) e pereiro (*aspidosperma pyrifolium*). *Revista Verde de Agroecologia e Desenvolvimento Sustentável*, 4, p. 1-11 (2009). (In Portuguese).
- Rosa, A. H., Desenvolvimento de metodologia para extração de substâncias húmicas de turfa utilizando-se hidróxido de potássio. MSc Dissertation, Instituto de Química da UNESP, Araraquara (1998). (In Portuguese).
- Rosa, A. H., Rocha, J. C., Furlan, M., Zara, L. F. and Santos, A., Oxidação das substâncias húmicas de turfa durante o processo de extração alcalina. Estudo espectroscópico na região do infravermelho e do visível. In: *Anais Assoc. Bras. Química*, 47(1), p. 25-28, Natal (1998). (In Portuguese).
- Rosa, A. H., Rocha, J. C. and Furlan, M., Substâncias húmicas da turfa: Estudo dos parâmetros que influenciam o processo de extração alcalina. *Química Nova*, 23(4), p. 472-476 (1999). (In Portuguese).
- Rosa, C. M., Castilhos, R. M. V., Vahl, L. C., Costa, P. F. P., Effect of fulvic acids on plant growth, root morphology and macronutrient uptake by oats. In: *Humic Substances and Soil and Water Environment, 2004*, São Pedro, Proceedings... São Pedro: Embrapa Instrumentação, p. 207-210 (2004).
- Saito, B., Avaliação do processo de extração de substâncias húmicas da turfa através de extração alcalina para produção de fertilizante organomineral para solo. MSc Dissertation, IPT – Instituto de Pesquisas Tecnológicas do Estado de São Paulo (2012). (In Portuguese).
- Santos Jr., L. F. dos, Estudo das frações no processo de extração alcalina de substâncias húmicas da turfa. MSc Dissertation, Universidade Federal do Rio Grande do Sul (2003). (In Portuguese).
- Silva, R. M., Produção e qualidade da alface hidropônica cultivada com adição de substâncias húmicas. PhD Thesis, Universidade Federal do Rio Grande do Sul (2001). (In Portuguese).
- Spedding, P. J., Peat (Review). *Fuel*, 67, p. 883-899 (1988).
- Stach, E., Mackowsky, M.-Th., Teichmuller, M., Taylor, G. H., Chandra, D., Teichmuller, R., Stach's Textbook of Coal Petrology. Borntraeger, 2nd Ed., Berlin (1975).
- Stevenson, F. J., Humus Chemistry: Genesis, Composition, Reactions. John Wiley & Sons, 2nd Ed. New York (1994).
- Tsutsuki, K. and Kuwatsuka, S., Chemical studies on soil humic acids: I Elementary composition of humic acids. *S. Soil Sc. Plant Nutr.*, 24, p. 337-347 (1978).
- Varanini, Z., Pinton, R., De Biasi, M. G., Astolfi, S. and Maggioni, A., Low molecular weight humic substances stimulate H⁺-ATPase activity of plasma membrane vesicles isolated from oat (*Avena sativa* L.) roots. *Plant and Soil*, 153, p. 61-69 (1993).
- Wang, Y., Combe, C. and Clark, M. M., The effects of pH and calcium on the diffusion coefficient of humic acid. *Journal of Membrane Science*, 193 (1), p. 49-60 (2001).
- Yamamoto, S., Honna, T., Sanatani, N., Iimura, K., Influences of extracting temperature on diluted sodium hydroxide soluble humus properties, 2: Denaturation of humus extracts caused by the heating extraction in boiling water. *Pedologist (Japan)*, 38(2), p. 31-38 (1994).