

Effects of extraction and fractionation time on the yield of compost humic acids

O. H. AHMED

M. H. A. HUSNI

A. R. ANUAR

M. M. HANAFI

Department of Land Management
Faculty of Agriculture
University Putra Malaysia
43400 Serdang
Selangor, Malaysia

Abstract The yield of humic acids (HA) partly depends on the period of isolation (extraction and fractionation), extractants used, and conditions such as temperature, pre-treatments, and compost:extractant ratios of extraction. This study was conducted to investigate whether a relationship could be separately established between extraction time, fractionation time, and the yield of HA from composted pineapple (*Ananas comosus*) leaves, as well as the relationship between both variables (extraction time and fractionation time) on the yield of HA from this compost. Standard procedures (with some modifications) using 0.1M NaOH were used to isolate HA from compost. Although there was a quadratic relationship between extraction time and HA yield, there was no relationship between fractionation time and HA yield. This observation enables the isolation of HA of compost within 24 h or less instead of the existing average time of 48 h, hence helping in facilitating the idea of producing potassium humate as a foliar potassium (K) fertiliser from composted pineapple leaves and related crop residues instead of open burning, a practice that has undesirable environmental effects.

Keywords pineapple leaves; trend analysis; humic acid; compost

INTRODUCTION

The isolation of humic acid (HA) from soils and organic substances such as composts involves extraction and fractionation. The yield of HA depends on the period of isolation, and also on the extractants used and conditions such as temperature, pre-treatments, and compost:extractant ratios of extraction (Bremner & Lees 1949; Goh 1970; Goh & Reid 1975; Gracia et al. 1993). The extraction and fractionation periods of these acids varies from 4 to 48 h (Goh 1970; Goh & Reid 1975; Kakezawa et al. 1992; Stevenson 1994; Tan 1996) even though an extraction time of 24 h (Schnitzer & Preston 1986; DeNobili et al. 1990; Inbar et al. 1990; Amalfitano et al. 1995) is the usual practice. For fractionation time, it ranges between 12 and 24 h (Schnitzer & Preston 1986; Kakezawa et al. 1992; Stevenson 1994) although most studies usually use 24 h (Schnitzer & Preston 1986; Inbar et al. 1990; Stevenson 1994; Ahmed et al. 2004).

It is known that the yield of HA from soils increases with increasing extraction time (Stevenson 1994). However, no relationship has been established between HA yield and time of extraction or fractionation time, not to mention the relationship between these two variables and HA yield from composts, relationships that enable the estimation of the maximum and optimum HA yield with extraction or fractionation or both procedures. These relationships are particularly important for composted pineapple (*Ananas comosus*) leaves from which potassium humate used as a foliar potassium (K) fertiliser (38% K) has been produced (Ahmed et al. 2003) to discourage pineapple growers in Malaysia from *in situ* burning of pineapple leaves on peat, hence encouraging the recycling of this residue in an environmentally friendly manner. As much as 7 t/ha is openly burnt before subsequent replanting, but this practice does not improve K uptake and fruit yield of pineapple (Ahmed et al. 1999). Besides, Malaysia is one of the heaviest users of K fertilisers in the world (AGRIQUEST 1999/2000). It is even thought that it is the only country in the world with

a higher K requirement than a nitrogen (N) requirement. For instance, from January to September in 1998, the potassic fertilisers import bill was estimated at US\$115.58 million (AGRIQUEST 1999/2000). The aforementioned value-added approach is one of the strategies the country is adopting to reduce this high import bill. The shorter the HA extraction time for composted crop residues also provides one way to diminish the environmental pollution through open burning of pineapple residues, a practice that caused a total economic loss of US\$4.475 billion to Indonesia, Malaysia, and Singapore during the 1997/98 haze and fire catastrophe in South East Asia (Hon 1999; Mohd Shawahid 1999; Ruitenbeek 1999).

The objective of this study was to investigate whether a relationship could be separately established between extraction time, fractionation time, and the yield of HA from composted pineapple leaves. The extractant used was 0.1 M NaOH at 1:10 compost extraction ratio. These relationships enable the estimation of the extraction time or fractionation time for maximum yield of HA.

MATERIALS AND METHODS

The compost used in this study was from composted pineapple leaves (described in a previous publication (Ahmed et al. 2003)). The HA extraction was conducted using the procedures described by Stevenson (1994) and Ahmed et al. (2004) with some modifications. Five gram (dry-weight basis) compost samples at natural moisture content were placed into polyethylene centrifuge bottles and 50 ml 0.10M NaOH solution was added and the bottles stoppered tightly with rubber stoppers. The samples were equilibrated at room temperature on a reciprocal mechanical shaker, the inner sides of the bottles (at the end of each shaking period) were washed down with distilled water (ensuring no compost particle remained in these inner sides before centrifuging) (Stevenson 1994), and the samples centrifuged at 7500 rpm for 12 min. The dark-coloured supernatant liquors were decanted, filtered through glasswool, the pH of the solutions adjusted to 1.0 with 6N HCl, and the HA allowed to stand at room temperature. These steps were carried out under N₂ atmosphere (flushing of polyethylene centrifuge bottles with N₂) to minimise chemical changes in the extracted organic matter (Stevenson 1994). The extraction periods used were 4 (EP4), 8 (EP8), 12 (EP12), 16 (EP16), 20 (EP20), and 24 (EP24) h.

The fractionation periods used immediately after acidification were 3 (FP3), 6 (FP6), 9 (FP9), 12 (FP12), 15 (FP15), 18 (FP18), 21 (FP21), and 24 (FP24) h. At the end of each fractionation period, the excess supernatant liquors (fulvic acid) (Aiken et al. 1985) were siphoned off from the acidified extracts. The remainder of the suspensions containing the HA were transferred to polyethylene bottles, and centrifuged at 7500 rpm for 10 min. The HA samples were purified following a modification of the method of Ahmed et al. (2004) by washing them in 50 ml of distilled water through centrifugation at 7500 rpm for 10 min to reduce mineral matter (e.g., sodium (Na)) and HCl (used during acidification). This procedure was repeated five times after which the washed HA samples were oven dried at 30°C to a constant weight, weighed, and yields expressed as percentage by weight of HA in the compost used. The ash content, elemental composition, functional groups, and spectral characteristics of the HA samples isolated from the composted pineapple leaves of this study can be found in Ahmed et al. (2004). It must be noted that the complete process (extraction and fractionation) for this study was replicated three times, hence values used in this work were the means of these replications.

The relationship between extraction time, fractionation time, and the yield of HA, as well the relationship between both variables (extraction time and fractionation time) on the yields of HA, were evaluated using the statistical analysis system (SAS) version 8.2.

RESULTS AND DISCUSSION

There was a quadratic relationship between extraction time and HA yield (Fig. 1) from the pineapple compost studied, a result consistent with several observations (Bremen & Lees 1949; Goh & Reid 1975; Tan 1996) that the yield of HA increases with extraction time. Besides slowing down depolymerisation of high molecular-weight complexes (Stevenson 1994), the solubilisation of the compost increased with increasing time. This is because the exchange process of Na ions at the exchange sites (carboxylic, phenolic functional groups, etc.) of compost progressed with the extraction time until 19 h, a period when most of these sites might have been saturated with Na ion, making the compost highly soluble and hence the maximum yield at this extraction time. Another reason could be the difficulty of extracting the humic substances in the

Fig. 1 Relationship between extraction period (EP) and humic acid (HA) yield.

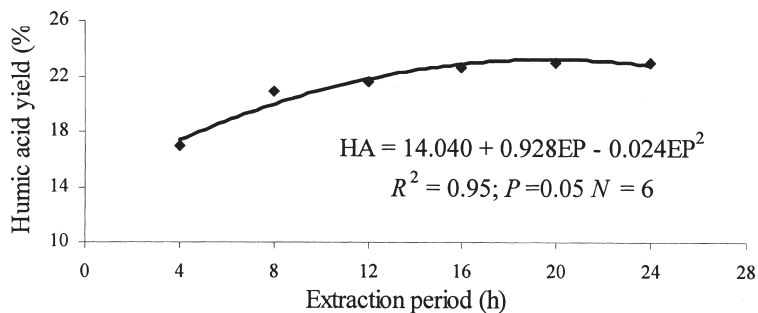
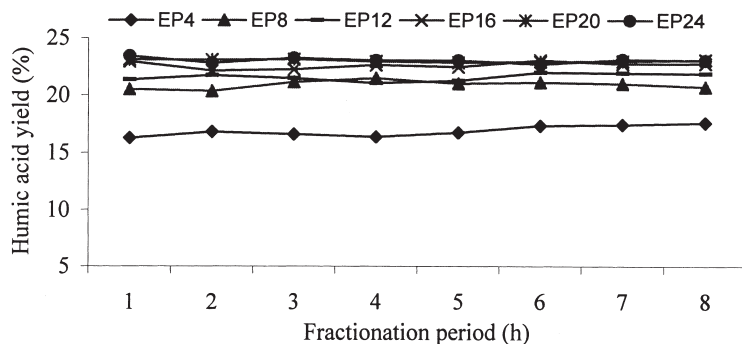


Fig. 2 Performances of fractionation periods under different extraction periods (EP) (no significant relationship $P=0.05$ between different fractionation periods and yield of humic acid for different extraction periods studied).



initial shorter period (e.g., 4 h) because of the difficulty of wetting the compost, as pineapple leaves are hydrophobic because of their waxy cuticles. It must, however, be pointed out that where the characterisation of the HA is of primary importance instead of the amount of HA isolated, an optimum extraction time (less 10% of maximum extraction time of 17 h; equivalent to optimum yield of 22.9%) or less could be considered, as the longer the extraction period, the greater will be the chemical changes (Stevenson 1994). Optimum extraction time was calculated as 90% of the maximum extraction time corresponding to HA yield of 22.9%, beyond which this yield will not be significantly different time-wise from the maximum yield and, for that matter, economically unjustifiable.

In contrast to period of extraction, no significant relationship was found between the period of fractionation with yield of HA (Fig. 2) for all periods of extraction studied, indicating that the yield of HA was not affected by fractionation time. Therefore, it is assumed that the minimum fractionation time in this study is 3 h, as this fractionation time was sufficient for the H ions to displace Na ions and other cations so as to saturate the exchange complexes of the HA immediately after acidification of the extracted humic and fulvic acid solutions or the supernatant.

CONCLUSIONS

The nature of the relationship between period of extraction and yield of HA from composted pineapple leaves studied is quadratic. The maximum and optimum HA yields can be obtained at extraction periods of 19 and 17 h, respectively. There is no relationship between period of fractionation and yield of HA, so from an economic point of view 3 h is sufficient to equilibrate HA immediately after acidification only for this compost. The significance of this study is that HA of compost can be isolated within 24 h or less instead of the existing average time of 48 h, hence facilitating the idea of producing potassium-humate (K-fertiliser) from composted pineapple leaves instead of open burning of these leaves, a practice that has undesirable environmental effects.

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