

Characterization of Organic and Organomineral Liquid Fertilizers

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1. INTRODUCTION

Use of organic and organomineral fertilizers has increased very much in Brazil and the world in the last two decades. In Brazil, this rapid increase in the demand for these products leads the Ministry of Agriculture, Livestock and Food Supply to search for new methodologies for the verification of their quality. This work aims to obtain information about the nature of these fertilizers.

2. MATERIALS AND METHODS

Six samples of liquid organic fertilizers commercialized in Brazil were selected, being made of different raw material. Density, pH, electric conductivity, and total solids in the commercial samples (Table 1) were determined. Additionally, aliquots of commercial products were lyophilized for elementary, thermogravimetric, and infrared analysis.

Table 1. Characteristics of liquid organic and organo-mineral fertilizers

| Samples | Classification | Origin material | pH* | Density (g cm ⁻³) | Total solids (g L ⁻¹) | Electric Conductivity**, (dS m ⁻¹) |
|---------|----------------|-----------------|-------|-------------------------------|-----------------------------------|--|
| L1 | organomineral | Leonardyte | 9.96 | 1.15 | 412.06 | 0.01 |
| L2 | organic | Leonardyte | 10.68 | 1.11 | 267.20 | 0.01 |
| P1 | organic | Peat | 9.30 | 1.17 | 514.22 | 0.03 |
| P2 | organic | Peat | 10.38 | 1.03 | 95.60 | 0.00 |
| H1 | organomineral | HOR*** | 4.84 | 1.17 | 531.32 | 0.02 |
| H2 | organic | HOR*** | 3.49 | 0.88 | 253.16 | 0.01 |

*dilution 1:10; **dilution 1:100; *** Hydrolyzated organic residues.

The humic acid fraction of each product was extracted according to the methodology of the International Humic Substances Society. Humic acids extracted and the lyophilized solid portions of the commercial products were analyzed by using the elementary analyzer (CHN), Perkin-Elmer CHNS/O 2400, employing 5 mg ± 0.100 mg of sample.

Samples of humic acid were also analyzed by thermogravimetry, with aliquots of 3-4mg in a DP Union TGA Q-500 thermo-analyser, under synthetic air atmosphere at a flow of 60 mL min⁻¹. The FTIR spectra in the region of the infrared of humic acids were

obtained in a Perkin-Elmer Spectrum One infrared spectrometer in pellets of KBr (mass proportion of 1:200).

Speciation of the most reactive functional groups present in the sample of humic acid was made with potentiometric titration. The experimental data were analyzed by using the Best7 program (4). The distribution of species was determined with the SPE and SPELOT programs (2).

3. RESULTS AND DISCUSSION

The determined pKas values (Table 2) could be attributed to carboxylic groups (phthalic and acetic acids), phenolic acids (phenol and catechol) and salicylic acid (1). After speciation of the organic molecules present in the samples, carboxylic acidity was observed to be predominant. This characteristic is important, since carboxylic groups are more active in tropical soils (3).

Table 2. Potentiometric titration data of the samples of organic and organomineral fractions of fertilizers

| Sample | Sites | pKa | % | Acid | mmol/g | Total acidity (mmol g ⁻¹) | Predominant Acidity |
|--------|-------|-------|----|-------------------------------|--------|---------------------------------------|---------------------|
| L1 | S1 | 4.77 | 46 | Phtalic Catechol Phenol | 0.532 | 1.152 | carboxylic |
| | S2 | 7.21 | 23 | | 0.262 | | |
| | S3 | 9.48 | 18 | | 0.205 | | |
| | S4 | 10.34 | 13 | | 0.153 | | |
| L2 | S1 | 4.75 | 44 | Phtalic Phenol | 0.516 | 1.181 | carboxylic |
| | S2 | 6.52 | 21 | | 0.248 | | |
| | S3 | 10.09 | 35 | | 0.417 | | |
| P1 | S1 | 5.10 | 43 | Phtalic Phenol | 0.314 | 0.734 | carboxylic |
| | S2 | 7.69 | 30 | | 0.217 | | |
| | S3 | 9.55 | 28 | | 0.203 | | |
| P2 | S1 | 4.90 | 62 | Phtalic catechol | 0.419 | 0.671 | carboxylic |
| | S2 | 6.88 | 17 | | 0.117 | | |
| | S3 | 9.28 | 20 | | 0.135 | | |
| H1 | S1 | 4.44 | 31 | Acetic catechol | 0.615 | 1.981 | Phenolic |
| | S2 | 9.07 | 69 | | 1.366 | | |
| H2 | S1 | 4.18 | 48 | Acetic catechol | 1.408 | 2.932 | carboxylic |
| | S2 | 6.44 | 27 | | 0.777 | | |
| | S3 | 9.09 | 25 | | 0.747 | | |

Despite being materials of different origin, the results of the elementary analysis (Table 3) have showed level of carbon with narrow range among the samples. This difference is even smaller in purified humic acid. However the level of nitrogen presented a wide range among the samples. The samples P1, P2, H1 presented significant differences between the amount of nitrogen in the commercial lyophilized product and purified humic acid. This fact could be explained by the addition of nitrogen to the fertilizer in its manufacturing process. Through the analysis of the H:C atomic relation, it was possible to separate the samples with contrasting characteristics. Purified humic acids of the same

raw material present a similar atomic ratio. Leonardite and Peat-based fertilizers presented low H:C relation while hydrolysed-based fertilizers showed a high H:C relation. This higher H:C ratio is related with aliphatic chains and this is usually related to a higher biodegradability of these substances. It was also observed a high C:N ratio in the purified humic acids of the samples of fertilizers with leonardite as the origin material.

Table 3. Amount of carbon, hydrogen and oxygen of the commercial lyophilized product and in the corresponding humic acid determined by the elementary analysis

| Sample | Lyophilized commercial Product | | | | | Purified Humic Acid | | | | |
|--------|--------------------------------|------|-------|------|-------|---------------------|------|------|------|-------|
| | C% | H% | N% | H:C | C:N | C% | H% | N% | H:C | C:N |
| L1 | 33.79 | 4.52 | 0.93 | 1.61 | 36.33 | 54.19 | 4.64 | 0.69 | 1.03 | 91.63 |
| L2 | 42.74 | 5.39 | 0.75 | 1.51 | 66.48 | 64.43 | 5.24 | 1.05 | 0.98 | 71.59 |
| P1 | 23.74 | 5.43 | 24.44 | 2.74 | 1.13 | 54.19 | 4.75 | 2.37 | 1.05 | 26.68 |
| P2 | 29.07 | 4.56 | 13.81 | 1.88 | 2.46 | 57.66 | 3.94 | 1.75 | 0.82 | 38.44 |
| H1 | 32.51 | 6.83 | 23.25 | 2.52 | 1.63 | 47.96 | 6.28 | 8.02 | 1.57 | 6.98 |
| H2 | 29.41 | 5.89 | 4.54 | 2.40 | 7.56 | 49.30 | 8.90 | 6.15 | 2.17 | 9.35 |

Hydrolysed-based fertilizers had a predominance of organic composts thermodegradable below 200°C. On the other hand, the samples of leonardite and peat-based fertilizers had thermal decomposition of their composts at temperatures between 400 and 500°C, hence explaining a higher recalcitrance of these compounds (Figure 1).

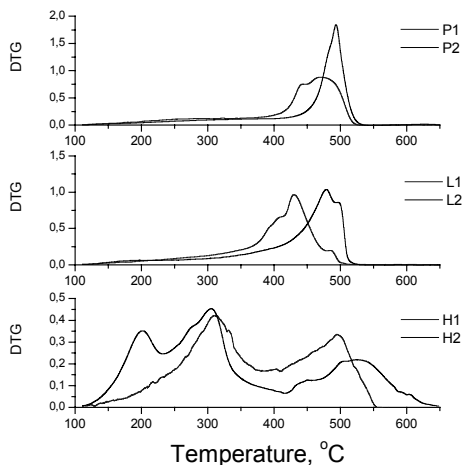


Figure 1. Thermogravimetric curves of the first derivative of HA extracted from fertilizers based of leonardite (L1 e L2), peat (P1 e P2) and hydrolysed composts (H1 e H2).

The infrared spectra of these samples of fertilizers of the same origin material presented similar characteristics. Peat-based samples presented peaks characteristic of carboxylic and aromatic groups; and predominance of hydroxyl. The hydrolysed-based samples presented characteristic peaks of aliphatic compounds (2940; 2840; 1470 cm^{-1}),

amide ($1540\text{-}1500\text{ cm}^{-1}$; $1080\text{-}1034\text{ cm}^{-1}$) and carbohydrates (2918 ; 2850 ; 1544 ; 1508 ; 1452 cm^{-1}). Leonardite samples have displayed spectra similar to those of peat. Peaks characteristic of aromatic groups and C-C bond in aromatic ring are predominant ($1548\text{-}1510\text{ cm}^{-1}$) (Figure 2).

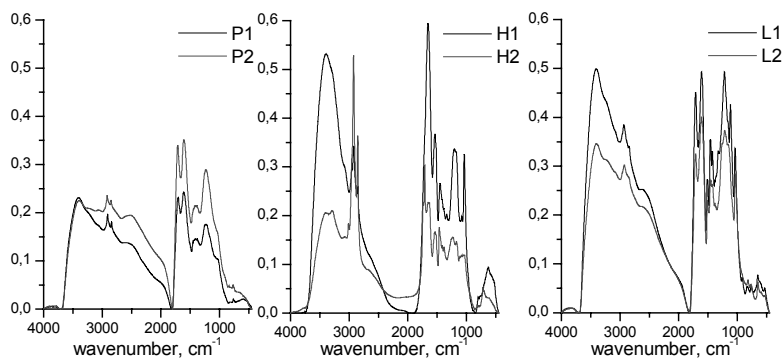


Figure 2. Infrared spectra of humic acid samples extracted from fertilizers based of peat (P1 e P2), hydrolysed composts (H1 e H2) and leonardyte (L1 e L2).

4. CONCLUSIONS

By the techniques employed for the characterization, fertilizers have presented distinct features. It was possible to identify the different compounds through them and to observe resemblances to samples of the same origin material. We have concluded that the information obtained trough those techniques can support the Ministry of Agriculture, Livestock and Food Supply, and contribute to a better standardization of organic and organomineral liquids fertilizers.

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