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Artigo

APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY, CHEMICAL AND CHEMOMETRICS ANALYSES TO THE CHARACTERIZATION OF AGRO-INDUSTRIAL WASTE

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Agroindustrial waste in general presents significant levels of nutrients and organic matter and has therefore been frequently put to agricultural use. In this context, the objective of this study was to determine the chemical composition, nitrogen, phosphorus, potassium, calcium, magnesium and carbon content, as well as the qualitative characteristics through Fourier transform infrared spectroscopy of four samples of poultry litter and one sample of cattle manure, from the southwestern region of Paraná, Brazil. Results revealed that, in general, the poultry litter presented higher amount of nutrients and carbon than the cattle manure. The infrared spectra allowed identification of the functional groups present and the differences in degree of sample humification. The statistical treatment confirmed the quantitative and qualitative differences revealed.

Keywords: poultry litter; cattle manure; organic matter; nutrients; multivariate.

INTRODUCTION

According to the Brazilian Institute of Statistics and Geography,[1] the Paraná state stands out nationally because of its agricultural and cattle breeding activities. Paraná is considered the major producer of poultry and the third largest milk producer in Brazil. Following the same trend, in the southwest region of Paraná State, raising of broiler chickens and breeding and raising of dairy cattle are economic activities of great significance. Due to the spread of these activities, the amount of waste produced is great, and the correct disposal of poultry litter and cattle manure has become one of the main concerns because of the associated environmental and agricultural problems that can result if disposal of this agricultural waste is not conducted in an appropriate manner and in amounts which are suitable for the soil.[2,3]

Poultry litter is distributed on the ground of confinement buildings to provide bedding for the poultry.[4] Poultry litter consists of a mixture of excreta, feathers, spilled feed and the material used to cover the ground. The composition of poultry litter, according to the Fertilization and Liming Handbook for the States of Rio Grande do Sul and Santa Catarina,[5] varies significantly according to the origin of the material, the animal species, the food used, the proportion of residues, the material used for bedding and the management of these organic materials. However, the chemical composition of the cattle manure depends mainly on the type of diet supplied to those animals.[6]

Because the constitution of such residues depends on different factors, the importance of chemical analyses prior to their use on the soil becomes very important, according to the Fertilization and Liming Handbook for the States of Rio Grande do Sul and Santa Catarina.[5] Amongst the chemical analyses, the nutrient determination stands out, as this determination allows the quantification of the essential elements that must be supplied to the soil for better development of plants. The quantification of organic matter (OM) is also important because the OM influence the chemical, physics and biologic characteristics of soil.[7] Other soil factors that are positively influenced by OM include cation exchange capacity, water holding capacity, microbial activity, soil tilth, soil structure, water and air infiltration, and soil temperature, and the OM reduces soil compaction and crusting and cements soil particles together which reduces erosion.[8]

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In addition to the quantification of OM, qualitative analysis can provide important information concerning the quality of the waste. The characterization by Fourier transform infrared spectroscopy (FTIR)[9,10] can offer important information about the humic acids, such as the presence of oxygen-containing functional groups and the purity with regard to inorganic contaminants. FTIR technique allows the identification of different chemical bonds among atoms through the rotational and vibrational deformations of bonds, which absorb energy at certain resonance frequencies depending on the characteristics of the atoms involved.[11,12]

This work therefore aims: (1) to determine, through chemical analyses, the nitrogen, phosphorus, potassium, calcium, magnesium and carbon (N, P, K, Ca, Mg and C, respectively) contents in poultry litter and cattle manure samples originating from farms located in the southwest region of Paraná State; (2) to characterize the OM in poultry litter and cattle manure samples using FTIR; and (3) to determine, through the use of statistical treatment, whether there are significant differences in the composition of the residues under analysis.

METHODOLOGY

Samples

The poultry litter samples were collected from four farms located in the southwest region of Paraná state. The residues designated R1 and R2 came from two farms located in the rural region of Coronel Vivida, and the residues designated R3 and R4 came from farm lands near Pato Branco. These residues are constituted by wood shavings, fecal samples and food scraps. Poultry litter were collected from barns in which chickens were being raised for meat production. The collect was realized in the early stage of the development of chickens. The cattle manure sample, designated R5, was collected from farm lands near Coronel Vivida. The samples analyzed comprised composed samples, collected from ten random points, mixed and homogenized. The collections were carried out in July 2013. Such waste, poultry litter and manure, was selected from the material often produced in the region, due to its economical activity, and also regarding the current environmental concern in the region because of the ways it has been disposed. Thus, after visiting some properties of the region, some were chosen which are giving a different destination to the waste, which constitutes agriculture disposal.

Sample preparation

After collection, the samples were dried in oven at 60 °C and later ground in a Wile knife mill.

Chemical analyses

The chemical analyses were carried out in the Soil Laboratory at the Universidade Tecnológica Federal do Paraná, at the Pato Branco campus. To determine nutrients (N, P, K Ca and Mg), the methodology suggested by Tedesco[13] was employed. This methodology enables the determination to be carried out with a single digestion involving a mixture composed of H_2O_2 and H_2SO_4. The total C contents of the samples were determined on 0.5 mg of sample by dry combustion using a Eurovector 3000 elemental analyser (Milan, Italy). This was done in duplicate for each sample.

Spectroscopic analyses

The poultry litter and cattle manure samples (R1, R2, R3, R4 and R5) were analyzed using FTIR (Spectrometer Frontier by Perkin Elmer, at the Universidade Tecnológica Federal do Paraná). Samples were compacted into KBr pellets (1.5 mg sample: 150 mg KBr). The spectra were obtained by scanning at 4000 to 400 cm^{-1} intervals, with 4 cm^{-1} spectral resolution.

Statistical treatment

Results obtained from the chemical analyses were subject to analysis of variance (ANOVA) and Tukey's test, at 5% significance. Results obtained from the chemical and spectroscopic analyses were subject to principal component analysis (PCA) and hierarchical cluster analysis (HCA). All statistical analyses were carried using the software Pirouett Version 4.0 (Informetrix, Seattle, Washington, USA).

The coefficient of variation (CV) was calculated using Equation 1:

$$CV = 100\left(\frac{s}{\bar{x}}\right) \quad (1)$$

where: s = *standard deviation;* $\bar{x}$ = *average*

RESULTS AND DISCUSSION

The results obtained through the chemical analysis of agro-industrial waste (poultry litter and cattle manure) are shown in Table 1.

Results obtained through the PCA statistical treatment, involving the results of chemical analyses of agro-industrial waste (Table 1) are shown in Figure 1A and 1B.

There were no significant statistical differences ($p > 0.05$) in the N and Mg contents of the samples at 95% confidence interval. The P content varied between 0.8% and 1.7%, but there were no statistically significant differences among the poultry litter samples. The P content by R5 cattle manure sample is different statistically of the samples by poultry litter R1 and R2. The potassium, K, content showed no significant statistical differences among the poultry samples, but there is significant difference between the R1 and R5 samples. The R3 and R4 showed higher Ca titers and these samples no differ of the R1 and R2 samples ($p > 0.05$). The cattle manure sample, R5, presented the lower Ca level, which differ of the all others samples. Carbon contents of the poultry litter samples were 10 times higher that carbon contents of the cattle manure sample. These last differ significantly by all the poultry litter samples.

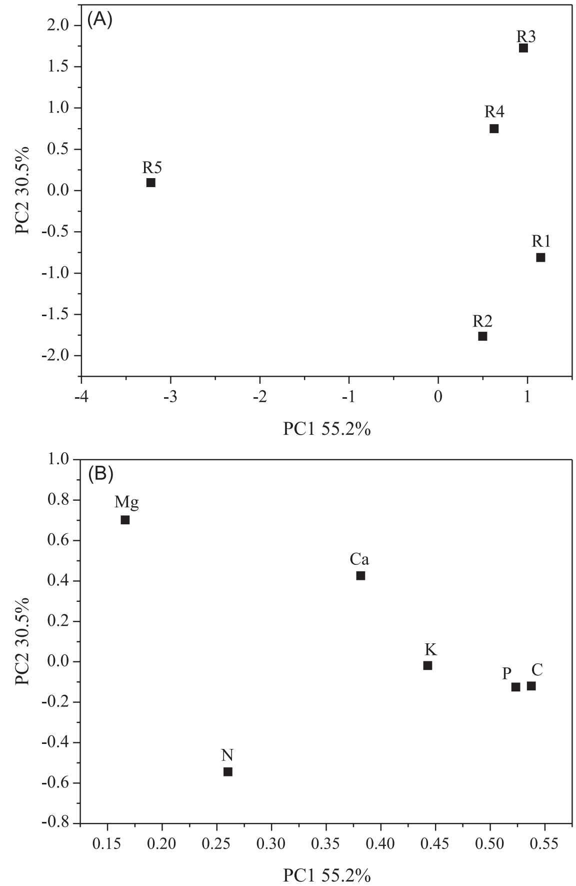

Figure 1. *Graph of the statistical analysis: PC1 versus PC2 (A) scores and (B) loadings, for the agro-industrial waste samples*

This result was confirmed by the PCA analysis (Figure 1A), which shows clear separation between agro-industrial waste according to PC1 (55.2%) and PC2 (30.5%). In addition to the difference observed between samples of the same type of agro-industrial waste, there is evidently a difference in the nutrient content when those samples (R1, R2, R3 and R4) are compared to the cattle manure (R5) (Figure 1A). From Figure 1A, two groups of agro-industrial waste, according to

Table 1. Results of the N, P, K, Ca, Mg and C content (%) of poultry litter (R1, R2, R3, and R4) and cattle manure (R5) samples. Means with the same letter, in the same column, do not differ statistically from one another ($p \leq 0.05$). Values in parentheses are standard deviations

Samples	N	P	K	Ca	Mg	C
R1	1.9^{a} (0.5)	1.7^{b} (0.1)	2.8^{b} (0.1)	1.4^{ab} (0.2)	0.4^{a} (0.2)	35.6^{b} (0.2)
R2	2.6^{a} (0.4)	1.4^{b} (0.3)	1.9^{ab} (0.1)	1.8^{ab} (0.2)	0.3^{a} (0.2)	37.2^{b} (0.6)
R3	1.5^{a} (0.1)	1.4^{ab} (0.2)	2.4^{ab} (0.2)	3.2^{b} (0.5)	0.7^{a} (0.6)	33.0^{b} (6.0)
R4	2.0^{a} (0.1)	1.4^{ab} (0.3)	1.7^{ab} (0.1)	3.2^{b} (0.9)	0.6^{a} (0.6)	33.0^{b} (3.0)
R5	1.4^{a} (0.1)	0.8^{a} (0.1)	1.2^{a} (0.8)	0.5^{a} (0.4)	0.4^{a} (0.2)	3.4^{a} (0.0)

PC1, one formed by the poultry litter and another by the cattle manure, can be observed. However, PC2 reveals better separation among the poultry litter agro-industrial waste. R1 and R2 (poultry litter residues) revealed a higher content of Mg and Ca than the other samples. The agro-industrial waste samples R1 and R3 exhibit a high K content. The R5 (cattle manure) exhibits lower values of N, P, K, Ca, Mg and C content than the other samples, as seen towards the left side in Figure 1A.

It is important to highlight that the results were obtained from the evaluation of a single sample of cattle manure, once only one of the properties visited used this residue as fertilizer. However, these results are still relevant, once the cattle manure does not present great variability in its composition and this is mainly due to the animal diet.[14]

The PCA analysis proved to be so sensitive that it could group agro-industrial waste R1 and R2 (from the same rural region of the Coronel Vivida city) separately from agro-industrial waste R3 and R4 (which come from the Pato Branco city farms). The results obtained by HCA (Figure 2) corroborate these results and reinforce the separation and clustering of agro-industrial waste. Similar results were observed in the literature.[15]

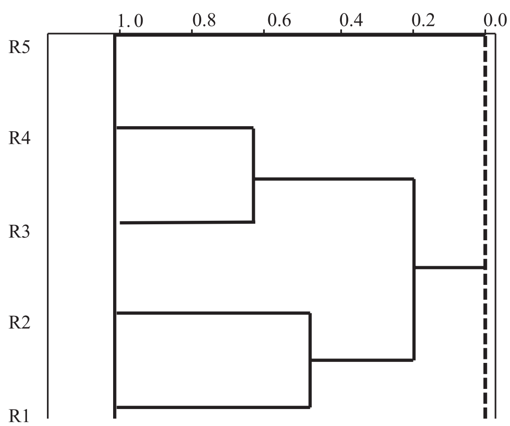

Figure 2. *Graph of the statistical analysis: agro-industrial waste sample HCA*

The HCA graph (Figure 2) shows similarity between the samples R3 and R4. R1 and R2 also presented similarities, but all poultry litter samples differ significantly from sample R5 (cattle manure). The separation among R1, R2, R3, R4 and R5 and the formation of three groups, one group comprising R1 and R2, another R3 and R4 and the third consisting of R5, previously observed through the PCA (Figure 1A), is reinforced.

According to Oviedo-Rondón[15] the variation of nutrients in different residues of poultry litter can be the result of several factors, amongst them the type of material used to generate the initial layer, the amount of material added between flocks, the number of flocks bred on that bedding, broiler mortality rate, storage time, and bedding removal (or failure to remove bedding) between breeding cycles. In this context, the separation of the poultry litter samples into two groups (Figure 1A) might result from these factors, except for the influence of the material used to generate the initial layer, once in all samples, R1, R2, R3 and R4, wood shaving was used. Therefore, the variations observed in the poultry litter waste composition are probably due to the remaining factors already pointed out by Oviedo-Rondón.[16] The formation of a distinct group formed only by the cattle manure sample (R5), however, makes more evident the difference resulting from the animal species in the residue composition.

Another relevant parameter that reinforces the idea of variability of N, P, K, Ca, Mg and C contents in animal manure is the calculation of relative standard deviation, commonly called the coefficient of variation, which measures the dispersion of data. Lima[17] and Severino[18] analyzed eleven and five organic materials, respectively, and observed that the content of each nutrient was different in relation to the type of agro-industrial waste. The CV calculated among poultry litter and cattle manure samples for N, P, K, Ca and Mg corresponded to 25.3, 24.5, 31.0, 58.2 and 34.2%, respectively. These values show dispersion in the nutrient content of each sample. The CV is a parameter often to measure the variability of the data.[2,15] However, according to the nutritional parameters plotted in Figure 1B, variations responsible for the separation among residues in the poultry litter and cattle manure were P, C and Ca. Because we compare agro-industrial waste according to these variables, it is possible to see the clear separation.

In general poultry litter samples (R1, R2, R3 and R4) presented a higher nutrient content than the cattle manure sample (R5) (Table 1). Severino[18] also obtained better results with poultry litter when compared with bovine manure residues and concluded that, regarding the eleven materials analyzed, poultry litter was among the top three in nutrient content.

Through the comparison between the N, P, K, Ca and Mg average results obtained for the poultry litter samples and those obtained by Lima[17] and Teixeira,[19] the N, P and Ca content present in the poultry litter analyzed is observed to be lower. Regarding K content in poultry litter, the value obtained is above the content determined by Lima[17] and below the content determined by Teixeira.[19] This result shows the variability in the chemical composition of the agro-industrial waste under analysis. Similar results are observed in the literature.[2] This result is confirmed when the behavior of Mg is observed, with similar results to the results found by Teixeira[19] but lower than the results presented by Lima[17] by residues characterization.

Comparison of the nutrient content in different samples of poultry litter confirms the variation observed in the composition of this agro--industrial waste, which (according to Oviedo-Rondón)[16] is influenced by several factors previously mentioned.

Table 2. Comparison among the nutrient contents of the cattle manure sample (R5) with others studies

Nutrients (%)	Cattle manure in this work	Lima *et al*. (2006)	Teixeira *et al*. (2002)
N	1.4 ± 0.1	0.77	2.01
P	0.8 ± 0.1	0.87	0.67
K	1.2 ± 0.8	0.32	1.52
Ca	0.5 ± 0.4	0.30	0.73
Mg	0.4 ± 0.2	0.18	0.56

From the data shown in Table 2, the N content found for the cattle manure is noticeably lower than the N content found by Teixeira[19] and higher than the value presented by Lima.[17] Regarding the P content, the converse is seen. The K and Mg contents are similar to those of Teixeira[19] but higher than the K and Mg content determined by Lima.[17] Values observed for Ca show that the cattle manure sample that was analyzed presented similar results than compared with Lima[17] and Teixeira.[19]

According to Barbosa,[6] this variability observed among the contents determined in this study and the contents described in the literature is due mainly to differences in animal diet.

Chemical characterization of residues of poultry litter and cattle manure revealed relevant results about their respective compositions, reinforcing possible contributions that they can provide to the plants when added to the soil as fertilizers.[8] However the agro-industrial residues generally should not be applied directly in the soil without prior stabilization by composting, vermicomposting, digestion, among others.[25,26] Such a contribution is cited in the literature by several authors such as Sbardelotto and Cassol[3] who observed that the use of poultry litter at corn plantations with and without soil coverage, resulted in high fertility soil and influenced both the plant height and the weight of a thousand grains. However, use of poultry litter did not influence grain yield. Silva[27] worked with the application of cattle manure on corn plantations and observed that the residue contributed to the increase in P and K content of the soil, in addition to improving water retention and enhancing productivity.

The C content, it was possible to verify that the poultry litter stood out when compared to cattle manure and by FTIR it is possible to characterize the OM present in the samples.

Others works in the literature reinforce the use of infrared radiation in the characterization of agro-industrial waste.[26]

The analysis was carried out in duplicate, but Figure 3 presents only one FTIR spectrum for each agro-industrial waste sample.

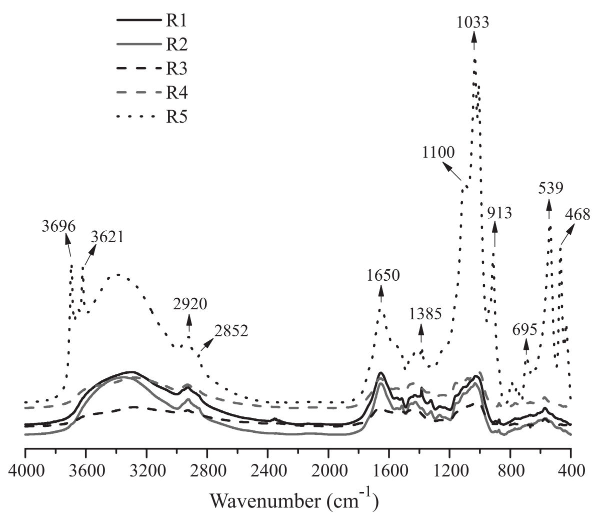

Figure 3. FTIR spectra of poultry litter samples, R1, R2, R3 and R4, and cattle manure R5

Table 3 is an adaptation from Benites[9] and presents some infrared absorption bands found in the literature for soil samples and humic acids, as well as their description.

In the cattle manure, peaks between 3696 and 3620 cm^{-1} (Figure 3) were observed that were not observed in the FTIR spectra of poultry litter residue, and these peaks might be ascribed to O–H axial deformations in kaolinite and gibbsite.

In all spectra (poultry litter and cattle manure), there is a wide and intense band in the region between 3032 and 3598 cm^{-1}, which is most likely the same band described by Pavia[21] but with a small displacement (Figure 3) that can be ascribed to O–H stretching vibrations of H bonded to OH groups and N–H stretching (Table 3).

The band at 2927 cm^{-1}, which was observed in all spectra, corresponds to the asymmetric deformation of methylene and methyl groups. This band indicates the presence of aliphatic chains in the samples. The peak present at 1650 cm^{-1}, also observed in all spectra, is in the region corresponding to the asymmetric deformation of carboxylate ions. The peak at 1385 cm^{-1} might correspond to the symmetric axial deformation of carboxylate ions, COO^-.[28]

For the cattle manure spectrum, intense peaks were observed at 1100 and 1035 cm^{-1}, which did not occur in the poultry litter spectra. However, these peaks are believed to be related to the signal observed at 1010 cm^{-1}, which occurs in all poultry litter spectra. This signal might be ascribed to the angular deformation of O-H. All of the samples also present a shoulder at approximately 1050 cm^{-1} that might represent the C-O axial deformation in polysaccharides or even the Si-O presence of silicate impurities.

The peak at 915 cm^{-1} in the cattle manure spectrum (which presents a small dislocation to the right) is less intense in the poultry litter spectra, most likely indicating the presence of aromatic compounds. According to Pavia,[21] the spectral region between the 900 and 690 cm^{-1} peaks corresponds to the out of plane folding of aromatic C-H. The higher intensity of this peak in the cattle manure sample spectrum shows that the C in this agro-industrial waste is richer in aromatic compounds than the C in poultry litter residue. This result might indicate a higher degree of humidification for the R5 compared to the other agro-industrial waste in this study.

Table 3. Infrared absorption regions observed in poultry litter and cattle manure samples, with respective descriptions and literature references

Frequency / cm^{-1}	Description	Reference
3695	O-H axial deformation in kaolinite	20
3620	O-H axial deformation in kaolinite and gibbsite	20
3500-3100	O-H stretching vibration linked by hydrogen bonds and N-H stretching of amines.	21
2918	C-H asymmetric axial deformation in methyl and methylene	22
1670-1620	Asymmetric axial deformation of anion carboxylate in covalent bond with metal; contribution of amide, ketone or quinone	23 24
1420-1400	Symmetric axial deformation of carboxylate anion	21
1080-1050	C-O axial deformation in polysaccharides	11
1030	Si-O axial deformation in kaolinite or O-H angular deformation in gibbsite	20
1010	O-H angular deformation in kaolinite and gibbsite	20
900-690	Out of plane folding aromatic =C-H	21
540	O-H angular deformation in kaolinite and gibbsite	20
470	Si-O deformation in kaolinite	20

The band which represents O-H angular deformation at 540 cm^{-1} (according to Russel)[20] might have suffered displacement in the sample spectra, explaining the band observed at 538 cm^{-1}. Such a band is also more evident in the spectrum corresponding to cattle manure. Intense peaks at 538 and 468 cm^{-1} were observed in the cattle manure.

Thus, the FTIR spectra showed significant differences among the waste poultry litter and cattle manure. Among these, the presence of peaks relating to the O-H ad Si-O deformation in kaolinite and gibbsite (3696, 3620, 538 and 468 cm^{-1}) which appear only in cattle manure, the difference in the intensity to the peak in 1035 cm^{-1} for the cattle manure compared to poultry litter. Others important differences can be observed too among the wastes, peaks in 915 and 1100 cm^{-1}, characteristic by aromatic =C-H and C-O axial deformation in polysaccharides, respectively (Figure 3).

These results indicate differences of the degree of humification of OM from residues, consequently it is expected to observed behavior among residues when applied to the soil.

Among the differences observed between the spectra, the most important ones regarding the OM humification are described by the absorption intensities in 2920 cm^{-1} (aliphatic groups) and 1630 cm^{-1} (aromatic groups). These groups are closely related to the OM humification process. According to Zech,[29] during the process of humification the main transformations occurring are loss of polysaccharides and phenolic moieties, modification of lignin structures, and enrichment in recalcitrant, non-lignin aromatic structures, thus, the humification is closely related to the OM decomposition and stabilization. Therefore, a residue with higher humification degree, that is, higher concentration of aromatic groupings in comparison to the aliphatic ones, will be more stable and will provide the soil with a slow release of nutrients, influencing its characteristics in a persistent and long-lasting way. The difference in the absorption intensities of these specific regions (2920 and 1630 cm^{-1}) of the sample FTIR spectra indicates, therefore, that the residues under evaluation present distinct characteristics regarding the humification degree. This observation is even more evident when the poultry litter and the cattle manure spectra are compared, the latter presenting more intense absorptions. All this influences the soil characteristics after the addition of each residue, mainly regarding the humification degree.

Qualitative comparison of the residues under analysis with other studies was not possible due to the lack of similar studies in the literature.

The statistical treatment of data obtained through FTIR spectroscopy had to be carried out separately for each absorption region because the program employed did not allow the use of all results at once. In this work, a score graph for the interval 1492 to 1300 cm^{-1} is presented (Figure 4). Despite being limited to only a small region of the spectrum (1492 to 1300 cm^{-1}), the graph shown in Figure 4 allows the confirmation of the OM difference in the residues analyzed. The statistical treatment carried out on the FTIR results allows the separation of the agro-industrial waste samples. According to PC1 and PC2, there was separation and clustering between the different agro-industrial waste according to the replication of analyses.

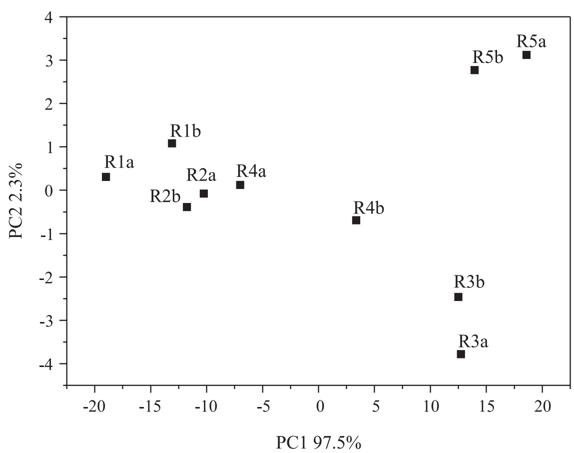

Figure 4. *Statistical analysis graph: PC1 versus PC2 scores of agro-industrial waste sample FTIR result. *As the results obtained were replicated, the letters (a) and (b) indicate the repetition of each sample.*

CONCLUSION

By chemical analyses, aided by the statistical treatment, it was possible to observe that the poultry litter samples presented a higher content of all nutrients and also C when compared to the cattle manure sample. Poultry litter can be considered to be better than cattle manure regarding the nutritional aspect (N, P, K, Ca and Mg). Samples of the same type of residue might vary significantly according to their origin, highlighting the importance of chemical analyses of these agro-industrial wastes prior to application to the soil.

Results obtained through the FTIR spectroscopy allowed characterization of the agro-industrial waste OM, indicating the functional groups present and their intensity. The spectra qualitative analysis allowed the observation of differences between the cattle manure and poultry litter samples, in relation to the aliphatic and aromatic groups, which are indicators of humification, stability and decomposition of residues.

By employing PCA, significant differences in the residue OM characteristics could be observed, indicated by the clear separation among the agro-industrial wastes.

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