

Physicochemical characterization of MSW from a bioreactor that simulates the conditions of a sanitary landfill

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ABSTRACT: Municipal solid waste are a mixture of different materials derived from human activities with a high potential cause of environmental impacts. Characterize in physicochemical terms a set of materials such as wastes is essential for knowledge and generating clues about its behavior under certain conditions, allowing also study ways to control or minimize its impact on the environment. This research aimed to characterize urban wastes produced in the city of Campina Grande (PB), based on residues deposited in a bioreactor that simulates a landfill conditions. Physicochemical techniques were used that the current technical standards, have allowed and defined the capacity obtaining data necessary to describe some characteristics of the studied material, with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG) and differential thermal analysis (DTA) chosen. The FTIR tests indicated the predominance of organic materials present in the wastes samples. By XRD patterns main peak and common to all samples was quartz, justifying the presence of soil covering the samples. The wastes samples have low thermal stability, with five stages of loss, from room temperature to 1000 °C, associated with volatilization of organic solvents, the combustion of cellulose, natural rubber, putrescible organic matter and plastic materials, as well as oxides formed during process, according TG and DTA.

KEYWORDS: Wastes, MSW, characterization, FTIR, XRD, TG, DTA.

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I. INTRODUCTION

In emerging countries such as Brazil, the range of problems related to municipal solid waste (MSW) is large and appears to be difficult to solve, since municipal managers – directly responsible according to the national wastes policy – do not seek investments for the sector [1]. The mass of waste generated grows every year, even with policies and educational campaigns that seek the opposite, due to factors such as disorderly and disorganized urbanization, in most cases, population growth, socio-economic development that generates a consumption profile of material goods - which will inevitably become waste - in people and ever shorter product life [2–4]. In Brazil, 3/5 of the wastes is, according to ABRELPE (2018) [3], destined to landfills, a little more than 1/5 to controlled landfills and almost 1/5 to dumps, being, the latter, enterprises with a high potential for environmental degradation.

Landfills comprise the most used technique for disposal of wastes in Brazil and the world, for offering the possibility of generation of energy by taking advantage of landfill gas (LFG), pollution control and for the operation considered simple, but generate a relatively large environmental liability, since they occupy large areas and because some projects do not meet sustainable criteria [5– 6].

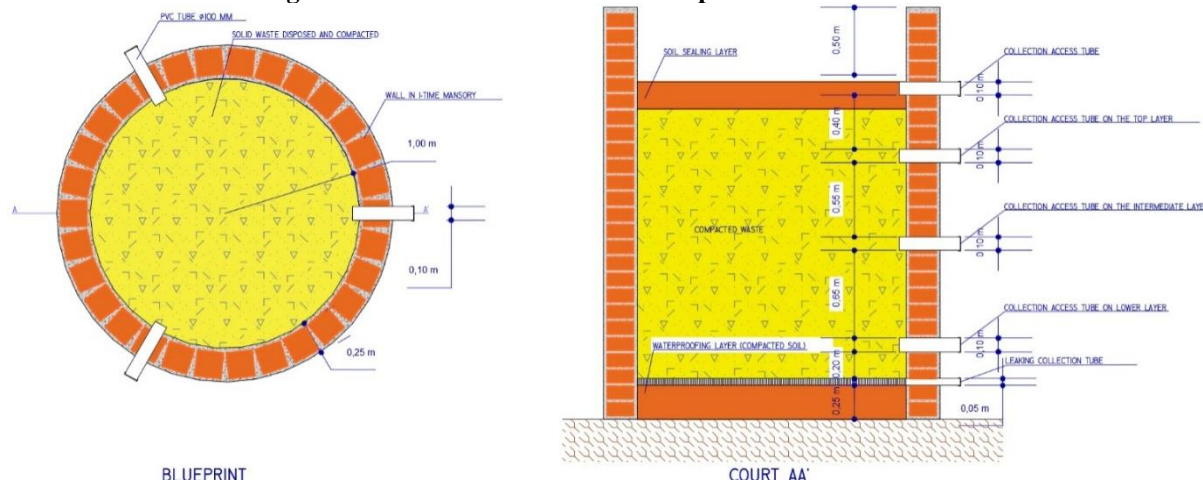
Table 1 shows gravimetric composition of wastes placed in the experimental bioreactor, according to the analysis performed by Ribeiro (2012) [7].

Table1 Gravimetric composition of wastes placed in the experimental bioreactor.

Fraction	Proportion (%)
Organicmatter	66.0
Paperandpaperboard	5.0
Plastics	11.0
Metals	3.0
Glass	4.0
Textilehealth	4.0
Composites	1.0

Figure 1 presents construction details of the experimental bioreactor installed at the UFCG (7°12'52" S, 35°54'21" W) that simulates landfills conditions (filled with wastes).

Figure 1. Construction details of the experimental bioreactor.



Residues placed in the bioreactor came from the mass collected in the city of Campina Grande and destined to the landfill installed in the city of Puxinanã (PB), that received about 400,000 ton month⁻¹ [8]. Firing conditions in the open in landfill and presence of housing units in this space, define operating conditions characteristics of dumps [9].

Physicochemical characteristics study of wastes allows a more detailed analysis of the composition and its thermal compartment, thus allowing point more appropriate allocation of sources for disposal of this material, aiming to reduce environmental impacts and use this.

Analyze physical and chemical characteristics of wastes produced in Campina Grande (PB) city, deposited in a bioreactor that simulates landfill conditions, was general objective. The specific objectives were: collect and prepare wastes samples from experimental bioreactor located in UFCG, representing material generated and collected in the city, use of X-ray diffraction (XRD) and absorption spectroscopy in the infrared Fourier transform (FTIR) techniques to identification of the components present in the samples and thermogravimetry (TG) and differential thermal analysis (DTA) to determine the thermal stability of the samples.

II. EXPERIMENTAL PROCEDURE

Sample group were collected in four different months and in sequence, naming them, respectively, MSW CG A, MSW CG B, MSW CG C and MSW CG D, on either side of bioreactor openings.

Sample treatment consisted of dry (in greenhouse for 6 days to about 100 °C), grinding (in an analytical mill Quimis, Q298A model) and sieved (mesh #20, which has equivalent 0.84 mm opening).

Physicochemical techniques were used that the current technical standards, have allowed and defined the capacity obtaining data necessary to describe some characteristics of the studied material, with XRD, FTIR, TG and DTA chosen.

The XRD patterns of the samples were performed on Shimadzu XDR-6000 equipment, with the analytical conditions scanning "2theta-theta" from 2° to 30°, goniometer speed of 2° min⁻¹, step 0.02, using the "fixed time" method and in aluminum sample holder.

The characterization by IR spectroscopy in the infrared Fourier transform was performed on a model spectrometer IR Spectrum 21, Shimadzu. To obtain the spectra were used potassium bromide (KBr) pellets of molecular weight 119 g mol⁻¹, 1% comp, vacuum pressed, in the region of absorption between 4000 to 400 cm⁻¹ with resolution of 4 cm⁻¹.

The XRD patterns and the spectrograms were analyzed following references who have worked with similar natures materials.

Tests related to stability thermal of samples were made using the following thermoanalytical methods: TG and DTA. Equipment used was SDT Q600 model Simultaneous TGA/DSC of TA Instruments brand, with simultaneous testing of TG and DTA. Masses were used 10 ± 1 mg, positioned in alumina crucible, for each of four samples (eight tests), starting from ambient temperature to 1000 °C at a heating rate of 10 °C min⁻¹, under N₂ dynamic atmosphere, in flow rate of 50 mL min⁻¹.

TG and DTA curves were analyzed in Application "TA Instruments Universal Analysis 2000". Thus, thermal stability was determined and the material behavior over test temperature range was examined as a whole and in its losses steps defined empirically.

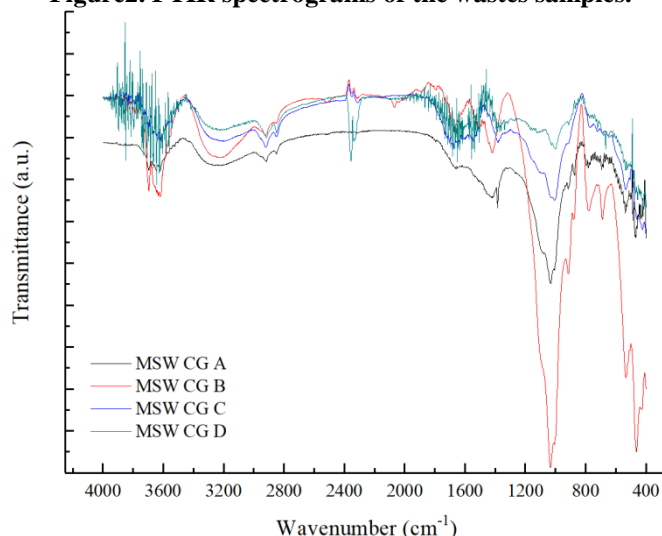
III. RESULTS AND DISCUSSIONS

3.1. FTIR of wastessamples

As a result of the tests absorption spectroscopy in the infrared Fourier transform two-dimensional graphs were generated defined as spectra, and the appropriate analyzes performed on these to identify the compounds present in the wastes samples collected in the bioreactor.

For an overview of the components of the wastes samples, Figure 2 shows the spectrograms of the four samples to indication of the functional groups to face track where there was the appearance of peaks or bands.

Figure2. FTIR spectrograms of the wastes samples.



Analyzing the spectra, according to references published studies materials by FTIR according tables that indicate the transmittance characteristic of each functional group, the main stretches have been identified in bands or peaks and to the functional group associated with the respective value.

Table 2 presents the analysis of data from the spectrograms of samples with wavelengths of identified strains and their association to the functional groups.

Table2 Data of FTIR spectrograms of wastes samples.

Functional groups found and respective wavenumber of stretching [cm-1]														
Samp	OH	N-H	C-H aliphatic	N=C=O	C=C=O	C=C	C=O of amides	CH2 adjacent to the carbon yl	C-H	C-O alcohols and phe	de RCH=C H2	Aromatic	Ethyl and propyl groups	-(CH2)n (n>3)
MSW CG A	3647; 3620	3273	2917; 2850	-	-	1659	-	1417	1384	1032	916	873	781	695; 688; 651; 628; 468; 428
MSW CG B	3690	3230	2922; 2853	-	2068	-	1671	-	1421	1034	1007	915	779	688; 651; 628; 464; 428
MSW CG C	3614	3196	2920; 2849	-	2313	-	1671	-	-	1088	1005	-	771	651; 628; 457; 423
MSW CG D	3730	3225	2917; 2848	2356; 2337	-	-	1651	1393	-	1069	1001	-	774	693; 668; 536; 485; 424

Being the mixture composed of wastes, largely of materials of organic origin, there is confirmation that the spectra of the samples of this material, in accordance with Leite (2008) [10], due to all have common bands of organic molecules.

The first three test samples resulted spectra peaks with seventeen or more specific bands, whereas the fourth (MSW CG D) due to noise might be pointed nineteen. Analytically, the four samples showed thirteen similar stretches, with small variations in wavelength.

The first four peaks of the samples occurred in a range $695 - 422 \text{ cm}^{-1}$, associated second Periotto (2012) [11], the angular deformation of the chain $-(\text{CH}_2)_n$ (for $n > 3$).

The peaks of the bands $790 - 730 \text{ cm}^{-1}$, $990 - 910 \text{ cm}^{-1}$ and $1200 - 1050 \text{ cm}^{-1}$, there has been one in each spectrum respectively represent the angular deformation of the ethyl group, the angular deformation out of the plane of the $\text{RCH}=\text{CH}_2$ functional group and the presence of primary and secondary alcohols [11–13].

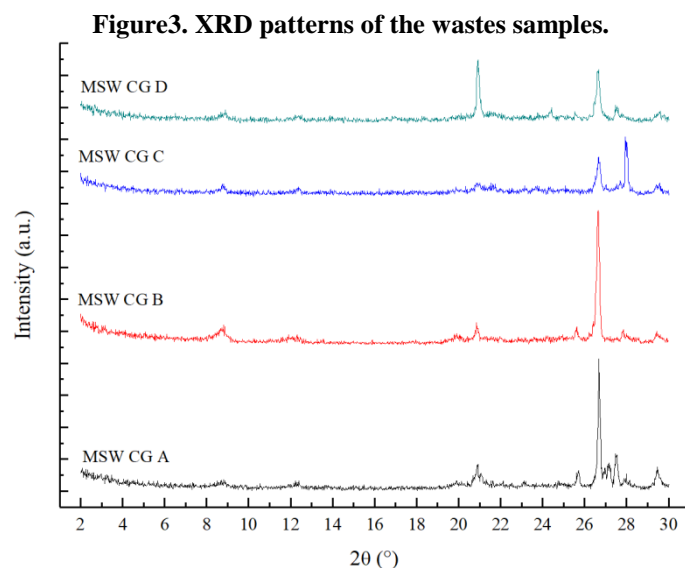
The transmittance area of $1500 - 600 \text{ cm}^{-1}$ is defined as fingerprint and samples of the same material must have equal bands and from these spectra should be similar [10]. Therefore, for the samples tested in this area were no differences in functional groups associated with the peaks, some with heteroatoms such as sulfur and nitrogen, in different intensities and small differences in wavelength, even showing the whole, a characteristic pattern.

In the area $3700 - 2850 \text{ cm}^{-1}$, according Leite (2008) [10], Periotto (2012) [11] and Pezzin (2010) [14], there are occurrences of peaks $-\text{O}-\text{H}$, $\text{N}-\text{H}$ and $\text{C}-\text{H}$ aliphatic respectively between $3600 - 3700 \text{ cm}^{-1}$, $3500 - 3070 \text{ cm}^{-1}$ and $2960 - 2850 \text{ cm}^{-1}$, bands where there are peaks in the spectra of wastes samples.

3.2 XRD of wastes samples

The X-ray diffraction test result provided four XRD patterns – graphics displayed in two dimensions with intensity peaks of diffraction occurring at a certain angle 2θ – one for each sample.

Figure 3 shows the XRD patterns of the samples MSW CG A, MSW CG B, MSW CG C and MSW CG D, determining of the peaks with intensities and width characteristics and analysis of the crystallinity peak of samples.



Analyzing the XRD patterns based on authors who have studied materials by XRD, major peaks in terms of the angle 2θ and relative intensities were identified as well as the crystallinity of the samples as shown in Table 3.

All diffraction patterns showed similar compartment, characteristic of amorphous material with some crystal phases present peaks, according Mundstock et al. (2010) [15], affirming prediction logic because they all samples of the same mixture of organic based materials.

The XRD patterns of samples MSW CG A and MSW CG B showed a peak of greatest intensity 2θ equal to 26.6 ± 0.05 degrees, having the same peak appeared in other samples, but they have a peak at each higher intensity this in 2θ equal to 27.94 and 20.93 degrees, respectively, in the samples collected in May and June.

The peaks observed in all samples $2\theta \approx 26,66^\circ$ indicate the presence of quartz (SiO_2), confirming the common peak in $2\theta \approx 20,92^\circ$ according Souza et al. (2003) [16], Martins (2009) [17], Bastos (2012) [18] and Cunha et al. (2014) [19], which is associated with the presence of covering soil of wastes in the bioreactor.

The peaks near $2\theta = 27,75^\circ$ are characteristic diffraction hematite (Fe_2O_3), according to Inda Junior et al. (2005) [20]. This characteristic has a phase of iron, indicating the presence of metals in samples fraction of wastes, and the constitution of the soil used in the coating of wastes in the bioreactor.

In terms of crystallinity, selecting the largest peaks of relative intensity values in the ranges $2\theta = 20^\circ$ to $2\theta = 21^\circ$ and $2\theta = 25^\circ$ to $2\theta = 29^\circ$, the larger the sample was identified MSW CG B (97.23%) while the lowest was in the sample MSW CG A (85.38%) with a mean of all samples of 92.24%. This is a given that guarantee the predominance of crystalline phases in the material constituting the wastes samples, but most of the XRD patterns presented as amorphous.

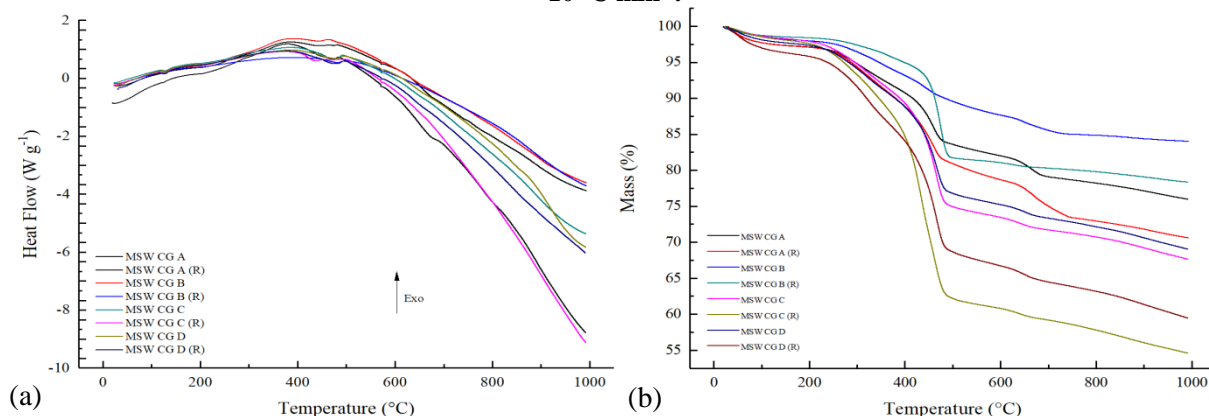
Table3Data of XRD patterns of wastes samples.

Sample	Identified major peaks					
	Amorphouspeaks	2θ (degrees)	I_{II}^{-1} (a.u.)	Crystallinity(%)		
MSW CG A	1	20,87	18,13	85,38		
	2	21,07	11,96			
	3	25,68	13,78			
	4	26,67	100,00			
	5	26,95	16,63			
	6	27,16	21,05			
	7	27,50	30,52			
	8	29,43	15,50			
MSW CG B	1	20,93	12,95	97,23		
	2	25,67	10,55			
	3	26,46	12,33			
	4	26,70	100,00			
	1	8,74	13,41			
	2	20,61	10,17			
	3	20,81	19,26			
MSW CG C	4	20,93	16,98	91,47		
	5	21,13	11,26			
	6	21,24	10,63			
	7	21,38	10,60			
	8	21,56	14,77			
	9	23,61	10,32			
	10	26,62	62,41			
	11	26,97	11,81			
	12	27,47	10,89			
	13	27,65	20,18			
	14	27,94	100,00			
	15	29,37	18,15			
	16	29,52	18,56			
	MSW CG D	1	8,75		10,24	94,89
		2	8,88		13,98	
		3	20,76		13,77	
4		20,93	100,00			
5		21,32	11,85			
6		21,52	13,13			
7		21,69	11,98			
8		24,40	15,25			
9		25,54	10,86			
10		26,64	90,14			
11		26,94	10,20			
12		27,51	22,72			
13		27,81	10,96			
14		29,57	16,16			
15		29,77	11,77			

3.3 Thermal Stability of RSU samples

Figure 4 presents TG (Figure 4a) and DTA (Figure 4b) curves of MSW CG A, MSW CG B, MSW CG C and MSW CG D samples, all with repetitions (R).

Figure 4. TG and DTA curves of wastes samples under N₂ atmosphere in 50 mL min⁻¹ and heating rate of 10 °C min⁻¹.



TG and DTA curves presented similar compartment (as Figure 4). Temperature increase caused five events with insignificant differences arising from the fact that material studied is a mixture, without guarantee of complete homogeneity and equality between samples.

From range of initial mass loss, between 24 °C and 166 °C, with peak at 48 °C is attributed 2.2% in weight of sample to the volatilization of organic solvents. In the DTA curve is identified as endothermic in a temperature, relative to solvents volatilization Laurenti and Maciel (2010) [21] and Duarte Junior et al. (2010) [22], Carneiro et al. (2013) [23].

Second event of mass loss, between 166 °C to 372 °C, with a peak at 331 °C, is related with burning of organic materials such as paper, rubber and wood and early thermal degradation of putrescible organic matter and plastics, characteristic of wastes composition and present in samples. The assertion is supported by Forteza et al. (2004) [24], which affirms that cellulosic matter has its ignition point (IP) at 250 °C, reinforced by Grammelis et al. (2009) [25] that amplifies this statement, and Sonobe et al. (2008) [26] for biomass between 180 °C and 600 °C, secured by Haykiri-Açma (2003) [27]. Caetano (2014) [28] which affirms that natural rubber has its self-burning started at 300 °C, Santana et al. (2013) [29] which confirms that organic matter starts burning at 300 °C, and Mortari et al. (2010) [30], Santos et al. (2011) [31] and Fallavena et al. (2013) [32] who affirm that volatile characteristic of organic materials are also eliminated in temperature range of that loss.

Third loss occurred between 372 °C and 592 °C, at 457 °C peak, is defined as extension of thermal degradation of organic, mainly organic matter fractions, the largest according gravimetric composition of sampled material which may be associated with higher mass loss, and plastics, since materials that fall into this class, low and high density polyethylene (HDPE and LDPE), polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP) and ethylene-vinyl acetate (EVA) have respectively 487–498 °C, 487–498 °C, 443 °C, 425–440 °C, 447 °C and 480 °C, with ignition temperatures in the range in which occurs that loss [33]. Second DTA curves, peaks at 386 °C, 467 °C, 484 °C and 573 °C are, respectively, exothermic, endothermic, exothermic and endothermic, characteristic of burn of the organic material (Silva, 2011) [34].

The last two events (592 °C to 738 °C and 738 °C to 991 °C) represent degradation of oxides formed in previous steps. The average of total loss was 26.7% or 73.3% of average residue.

IV. CONCLUSIONS

The spectrograms of FTIR indicate the presence of organic functional groups that impose the samples studied the condition of being formed primarily of organic materials, as could be predicted by studying the gravimetric composition performed previously to supply the bioreactor.

The XRD patterns indicated that the material is amorphous, characteristic of organic materials, with the presentation of intense crystalline peaks, as a mixture, and the samples having crystalline materials such as quartz and hematite (iron phase).

TG and DTA curves showed five steps of mass loss, with three endothermic reactions and two exothermic, corroborating that the material studied have low thermal stability, based on wastes samples, its capable of burning for energy and / or volume reduction.

Conflict of interest

There is no conflict to disclose.

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