Food waste stabilization and valorization by inorganic oxidative process

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Abstract:

Composting is a biological process and a relatively inexpensive way of treating OW, however, it requires large areas and usually takes 90 days to generate a final biostabilized product. Therefore, research into alternatives that allow the stabilization and valorization of organic wastes in shorter intervals of time can help to mitigate the environmental impacts allowing the recovery of part of the energy and natural resources used in soil conditioning and food production. The aim of this work was to investigate the applicability of a chemical advanced oxidation process for stabilization and valorization of canteen and restaurant food/kitchen waste (FW) in a time interval of one hour. The process is conducted in sequential batches and it is based on the traditional principles of inorganic chemistry, i.e. Bronsted-Lowry acid-base reactions and oxidation reactions. The results obtained allow us to state that the final product can be classified as a mixed organic fertilizer and may be sold or donated to small farmers or agricultural producers in accordance with the Normative Instruction number 25/2009 of the Brazilian Ministry of Agriculture Livestock and Food Supply. However, improvements in storage logistics to the avoid contamination of the material are still required, as well as more detailed investigations on agronomic aspects of the interaction of organic fertilizer with soil and plants.

Keywords: advanced oxidative process, composting, food waste, organic waste.

1. Introduction

In 2015 the urban organic waste production in Brazil was estimated to be 34 x 10^6ton per year. However, the valorization of the organic urban solid waste by composting process was only 0.2 %, while 64.6% was sent tolandfills and 33.2 % to open dump. Other valorization alternatives as: methane production by anaerobic digestion was adopted, in general, only in the huge landfills and the thermic process is still incipient.

The National Policy on Solid Waste, published by the Brazilian government in 2010, foresaw the need to implement organic solid waste composting systems and ways of using the compound produced through a deal with economic and social agents. Therefore, it is understood that the valorization of the organic fraction of the solid waste by composting, as well as the implementation of the selective collection and final environmentally adequate disposition are parts of the list of obligations of the Brazilian municipalities established by this Federal Law. However, when we consider the continental dimensions of Brazil, the deep regional disparities and the HDI of the majority of Brazilian municipalities, compliance with the regulations is a huge challenge.

Looking at the bright side, challenges also mean opportunities and the wide adoption of the composting process, mainly in the urban environment of large and medium-sized cities still depend on technological development and long term validation. Groslambert *et al*. (2016) exhibited an accelerated composting system that can transform food waste in valuable compost in only 24 hours. The researchers reported that the technology is based on a permanent control of the ratio of moisture and temperature, to optimize the biodegradation rate of food waste by a special consortium of more than thirty thermophilic bacteria. Nevertheless, some studies have demonstrated that the product obtained at the end of these processes is dry, but not bio-stable. Barthod *et al*. (2018) reported that immature composts have harmful effects on plant germination or development and also might cause environmental problems like water pollution and odours emissions.

The aim of this work was to investigate the applicability of a chemical advanced oxidation process for stabilization and valorization of canteen and restaurant food/kitchen waste (FW). Different solutions exist to manage this organic waste, for instance local and centralized composting, anaerobic digestion, or co-incineration with municipal waste. Except for local composting, these methods need to collect and transport the food waste to be processed, which mean transporting a lot of water (Groslambert *et al*., 2016). Our entire process occurred in a time interval of one hour and we also investigated if the quality of the final product (mixture) met the requirements of the Brazilian legislation

2. Material and Methods

The process is conducted in sequential batches and it is based on the traditional principles of inorganic chemistry, i.e. Bronsted-Lowry acid-base reactions and oxidation reactions. Four reagents (Bio-degrader – reagent A®, two Bio-activators – reagents A1® and A2®and a Bio-finalizer – reagent B®) which are elaborated with inorganic substances present in the soil and also in the digestive tract of some animals, are added to a mixture of food waste and sawdust.The organic fraction is degraded and a final product containing concentrations of macronutrients and micronutrients suitable for the development of agricultural crops is generated.

Canteen and catering food waste (50 kg per day) collected at the main Federal University restaurant, in Bahia state, Brazil, was triturated and mixed manually with sawdust observing a volumetric ratio of 10:3. The mixture (raw material) was transferred to a 150 kg concrete-mixer (reactor) and homogenized during 10 minutes. After mixing time, 7% by mass of a Reagent A® was added. So, the first step degradation lasted 10 minutes with a strong homogenization. Some Bronsted-Lowry/acid-base reactions occurred between the raw material and the Reagent A®. After this first reaction time, A-1® (an bio-activator) was added in the reactor at the ratio of 1.3 mL:kg of FW and homogenization was carried out for 20 minutes. Then, 35 mL of A-2® (another bio-activator) was added and mixed with the content of the reactor for 5 minutes. This step released heat and the temperature increased up to 45°C – 50°C. The next step of the inorganic oxidation process, that lasted 10 minutes, was the addition of the reagent B® (1 kg for 10 kg of FW) which seeked to increase the concentration of macro and micronutrients and make the material suitable for grinding. Finally, the mixture was withdrawn from the reactor, grinded and put to rest in a covered shed. After 24 h, 60 mL of A-1® was added again and manually mixed. A week later, the mixture was grinded again.

In order to evaluate the quality of the final product, samples were collected from the material withdrawn from the reactor immediately after the end of one batch and also at the end of 24, 48 and 72 hours. In addition, samples of material stored in the shed for maturation were collected at the end of 15, 30 and 60 days. Fresh samples were used for pH, moisture content, Coliforms and Helminths eggs analysis. The samples were dried for the determination of organic matter, carbon and nitrogen contents.

The pH value was determined with a pH meter equipped with electrodes using 1.0 g of the sample immersed in 50 mL of $CaCl_2$ (0.01M) and stirred for 30 minutes. Moisture content, organic matter and nitrogen were analyzed according to the Standard Methods for the Examination of Water and Wastewater. Nitrogen was determined by an adapted methodology of the 4500-Norg B method: 200 mg of the sample was placed in macro *Kjeldahl* flasks containing 1.0 mL of commercial H_2O_2, 700 mg of digestion mix (containing 100 g of Na_2SO_4, 10 g of $CuSO_4$.5H2O and 1.0 g of selenium) and 5.0 mL of concentrated H_2SO_4. The digestion was conducted in the speed digester system K-425 model, Büchi. After digestion, 50 mL of deionized water and 35 mL of 10 (mol.L^{-1}) NaOH were added to the sample, which was then distilled in 50 mL of boric acid, pH 4.65 in distillation unit K355, Büchi. Carbon was determined in a high-temperature solids combustion system (1,200°C) using Analytic Jena multi N/C®2100 analyzer. Total coliforms and *Escherichia coli* were quantified by defined substrate technique using Colilert®, IDEXX. Helminths eggs were quantified by EPA/625/R-92/0 methodology and Termotolerant Coliforms using SM9221. The concentrations of metals and other chemical elements were determined by using inductively coupled plasma-atomic emission spectrometry (USEPA 200.7 Method). The Cation-exchange capacity and Water-exchange capacity were also quantified.

3. Results and discussion

During the process of organic waste composting, one of the main concerns is the maintenance of temperature in values suitable for the inactivation of pathogenic microorganisms. According to Bustamante *et al.* (2008), three temperature ranges govern different biological aspects of composting: above 55°C maximize sanitization, between 45 and 55°C improve the degradation rate and between 35 and 40°C increase microbial diversity.The process evaluated in this work predicts that the reagents A1® and A2® should react primarily with the remaining amount of Biodegrader (reagent A®) that was not consumed in the first step. However, these bio-activators can also react with the organic fraction of the FW which in the formulation contains functional groups (RH, RSH, for example) by means of an advanced oxidative process and, then, form chemical species (radicals) according to three basic mechanisms: hydrogen abstraction, electronic transfer and electrophilic addition. Considering the occurrence of hydrogen abstraction, the resulting organic radicals are able to oxidize the FW through reactions that release heat and form CO_2, H_2O, humic substances and inorganic salts.Therefore, the maintenance of the temperature above 55ºC for a period of more than two weeks is explained, and it can be considered attractive, once that it allows obtaining a final microbiologically safe product. Besides, the process also met the more restrictive criterion established in the Brazilian environmental legislation which states that composting processes must remain at temperatures above 55ºC for a period equal or superior to 15 days.The temperature profile obtained during 15 days of monitoring can be seen in Figure 1. The evolution of the quality of the final product for seven days after the end of one batch can be seen in Table 1.

Fig.1 Temperature profile obtained during the first 15 days of monitoring

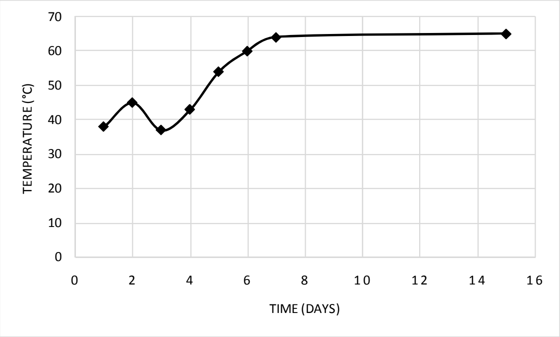


Table 1. Physicochemical parameters monitored after one batch of the oxidative process.

Step	pH	Moisture (%)	Organic Matter (%)	Carbon (%)	Nitrogen (%)	C:N ratio
Raw material	5.6	41.3	95.1	43.6	1.7	26.1
End of the process	12.1	44.9	75.5	34.4	1.6	22.0
After 24 hours	11.5	48.4	72.6	36.1	1.5	24.5
After 48 hours	9.3	50.2	72.0	30.8	1.3	24.4
After 72 hours	8.1	52.3	71.8	33.8	1.6	21.0
After 7 days	7.9	40.2	63.1	32.5	1.6	20.3

The physicochemical characteristics of the product obtained at the end of seven days of maturation is classified as mixed organic fertilizer and may be sold or donated to small farmers or agricultural producers in accordance with the Normative Instruction number 25/2009 of the Brazilian Ministry of Agriculture Livestock and Food Supply. However, it is necessary to quantify some micro and macronutrients and adjust the temperature for direct application to the soil. Figure 2 shows the aspect of the final product and Table 2 shows the values of physicochemical and microbiological parameters obtained in aliquots taken from four different piles of the final product under maturation and the requirements defined in the Brazilian environmental legislation

Fig.2 Evolution of the final product during the maturation period

Legend: a) Immediately after the end of the oxidative process; b) After one week at rest; c) After two weeks at rest

Table 2. Characteristics of the final product and limits required by the Brazilian legislation.

Parameters	Results				
	7 days	15 days	30 days	60 days	Regulation 25/2009 Class C*
Thermotolerant Coliforms (MPN/25g)	46,70 ± 64,06	851 ± 1.20	1	8,70 ± 10,32	< 1.1
Viable Helminths Eggs (egg/g TS)	927±1,24	0	0	0	<0.25

to be continued

Table 2. Characteristics of the final product and limits required by the Brazilian legislation (conclusion).

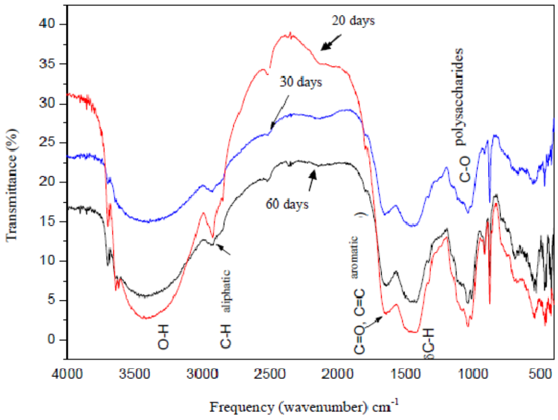
Parameters	Results				
	7 days	15 days	30 days	60 days	Regulation 25/2009 Class C*
Density (g/cm^3)	0.5 ± 0.0	0.5 ± 0.0	0.5 ± 0.0	0.5 ± 0.0	
Moisture Content 60 - 65°C (%)	40.2 ± 0.2	15.1 ± 0.2	13.5 ± 0.0	10.7 ± 0.0	
Moisture Content 110°C (%)	2.2 ± 0.1	3.4 ± 0.1	2.5 ± 0.5	3.7 ± 0.0	
Total MoistureContent (%)	42.4 ± 0.2	18.5 ± 0.3	16.0 ± 0.4	14.4 ± 0.0	70 (Máx.)
Total Organic Matter Combustion (%)	63.1 ± 1.9	65.5 ± 1.0	64.0 ± 0.0	67.0 ± 0.4	
Organic Carbon (%)	32.5 ± 0.0	33.8 ± 0.6	33.5 ± 0.0	35.1 ± 0.6	15 (Min.)
Insoluble Mineral Residue I. M. R. (%)	9.5 ± 1.8	11.3 ± 0.1	12.1 ± 0.9	8.4 ± 0.4	
Mineral Residue M. R. (%)	23.8±0.2	19.2±0.8	21.1±0.3	20.5±0.9	
Total Mineral Residue T. M. R. (%)	33.3 ± 2.0	30.5 ± 0.9	33.1 ± 0.6	28.9 ± 0.5	
Total Nitrogen (%)	1.6 ± 0.0	1.2 ± 0.0	1.2 ± 0.2	1.5 ± 0.0	0.5 (Min.)
Total Phosphorus (P_2O_5) (%)	0.3 ± 0.0	0.4 ± 0.2	0.3 ± 0.0	0.3 ± 0.0	
Total Potassium (K_2O) (%)	0.79 ± 0.6	0.4 ± 0.0	0.4 ± 0.0	0.6 ± 0.0	
Total Calcium (Ca) (%)	7.87	5.7 ± 0.2	6.1 ± 0.0	6.3 ± 0.7	
Total Magnesium (Mg) (%)	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	
Total Sulfur (S) (%)	0.07 ± 0.0	0.05 ± 0.0	0.07 ± 0.0	0.05 ± 0.0	
Water Retention Capacity (WRC)	176±19	150±4	147±3	157±8	
C/N Ratio	20.1±0.4	27.3±0.2	28.4±3.7	23.2±0.7	20 (Max.)

* This Regulation published by the Brazilian Ministry of Agriculture, Livestock and Supply in 2009 classifies as Class "C" the organic fertilizer that, in its production, uses any amount of raw material from urban solid waste.

High concentrations of Thermotolerant Coliforms can be attributed to the contamination of the piles during maturation of the final product. We realized that although our storage shed was covered, it allowed the entrance of small birds and that they might have deposited excreta on these piles. Some precautions are being taken to avoid this recontamination of the final product.

The use of the C:N ratio to evaluate the stability and maturity of the compost is quite controversial. Chefetz *et al*. (1998) state that the C:N ratio should be avoided for monitoring composting because it does not reflect the entire process. Spectroscopy in the infrared region was used for a preliminary evaluation of the presence of humic and fulvic substances in the final product. Samples were collected from three different piles at the end of 20, 30 and 60 days of maturation (Figure 3).

Fig.3 Infrared spectra – samples at the end of 20, 30 and 60 days of maturation



More detailed investigations on the use of infrared spectroscopy to investigate the maturity of the final product are still necessary, however, it can be stated that the spectrum obtained showed signs characteristic of the presence of humic substances and humic and fulvic acids (Fialho *et al*., 2010). The intensity of the signals around 1,660 cm^{-1} and around 2,910 cm^{-1} may be followed to illustrate the increase in carboxyl C formation, thus increasing the intensity of C=O and decreasing aliphatic carbon intensity. The broad band in the region of 3,500-3,300 cm^{-1} is attributed to the presence of O-H group. The signals at 2,910 cm^{-1} and one of lower intensity ("shoulder") at 2,850 cm^{-1} are designated as C-H stretch. There is still the presence of a signal around 1,660 cm^{-1} which may be due to the other C=O stretch, therefore the presence of carbonyl group, with a contribution of the C=C stretch.

The application of Inorganic Chemistry knowledge, focused on Bronsted-Lowry acid-base and redox reactions, can contribute to an innovative and effective process capable of significantly helping to decrease the amount of organic waste from food disposal in landfill and garbage dump sites. In the pilot plant at the Federal University of Bahia, Brazil, was produced more than 10 tons of this material. The applicability as organic fertilizer is being evaluated through physicochemical and microbiological analyzes. Complementary agronomic studies are also needed to evaluate the interactions of this material with soil and plants.

4. Conclusions

The stabilization of food residues through an inorganic oxidative process proved to be technically feasible and capable of generating a biostabilized final product and suitable for use as an organic fertilizer according to the criteria established in the Brazilian legislation.

Improvements in storage logistics to the avoid contamination of the material are still required, as well as more detailed investigations on agronomic aspects of the interaction of organic fertilizer with soil and plants.

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