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Use of Cassava Wastewater and Scheelite Residues in Ceramic Formulations

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Cassava Wastewater: An Introduction, Characterization and Potential

Jônatas Macêdo de Souza

Abstract This chapter contains a brief introduction on the need to reuse waste, presenting cassava wastewater as an effluent from producing flour and starch, which must be properly disposed of. The characteristics of cassava wastewater as well as its chemical composition and potential uses for reuse are discussed.

Keywords Agricultural waste · Ceramic formulations · Reuse

The growing exploitation of natural resources is becoming increasingly worrying due to the environmental impacts caused by extracting raw materials and the consequent inappropriate disposal of products at the end of their useful life. In view of this, the number of studies aimed at minimizing the effects resulting from degrading nature caused by various sectors of the economy has increased in recent years. A major challenge faced by researchers is to develop new, sustainable materials which reduce damage to ecosystems while meeting the requirements required by technical standards and environmental legislation.

It is interesting to differentiate between solid residues and wastes for a better understanding of the subject. In Brazil, Law No. 12,305/10 [1] defines solid residue as: "material, substance, object or discarded good resulting from human activities in society, whose final destination is proceeded, proposed to proceed or is obliged to proceed in the solid or semisolid states, as well as gases contained in containers and liquids whose particularities make its release in the public sewerage network or in bodies of water unfeasible, or require technical or economically unviable solutions in view of the best available technology." Furthermore, waste is defined as: "solid residues which, after all the possibilities of treatment and recovery by available and economically viable technological processes have been exhausted, do not present any possibility other than final and environmentally appropriate disposal."

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The concern with the correct destination of waste together with the problem of scarcity of raw material has stimulated several works with the use of these environmental liabilities in manufacturing ceramic materials; for example, Azevedo et al. [2] studied the effect of the glass residue on the rheological properties of the adhesive mortar, noting that mixtures with 10% replacement of cement and 15 and 20% replacement of aggregate, both concerning mass, presented better rheological characteristics; Nascimento et al. [3] incorporated granite cutting waste in plastering mortar and found that the mortar's mechanical properties were improved when the residue replaced the sand in the contents of 5, 10 and 20%; Spósito et al. [4] replaced part of the sand with PET bottle waste in the manufacture of hydrated Portland cement-based mortars and stated that this might be another possibility for disposal of the waste.

In other studies, Meena and Luhar [5] researched concrete produced with treated wastewater instead of potable water and found a compressive strength between 85 and 94% of the reference concrete; Yang et al. [6] analyzed the properties of foam concrete containing brick powder derived from construction and demolition waste and found that the residue could replace cement by weight by up to 15%; Siqueira et al. [7] verified the behavior of soil-cement bricks with eggshell and slag wastes and observed that the eggshell waste could replace mass cement by up to 30% and the slag residue could replace mass soil up to 15%; Islam et al. [8] used fly ash combined with cement to manufacture compacted earth blocks and verified that 7–8% cement and 15–20% fly ash concerning on the weight of the dry soil provide compressive strength and durability in terms of water absorption according to the standards of England and Australia. The results obtained in these studies of incorporating residues into ceramic formulations demonstrate that these mixtures are presented as alternative solutions for the correct destination of various environmental liabilities, as long as the wastes do not impair the technical properties required for using the materials.

Despite an extreme relevance, many economic sectors generate waste during the production process which are harmful to the environment when improperly disposed. This is the case in the agricultural sector in which the processing of some crops presents organic waste which needs further studies to determine the correct destination or reuse of this waste. One of these cultivars is cassava (*Manihot esculenta Crantz*), which has worldwide production of around 285 million tons/year of unprocessed roots, being the fifth most important basic crop in the world [9]. According to the Brazilian Institute of Geography and Statistics [10], Brazilian production of cassava root was around 19.4 million tons in 2018, which places Brazil as the fourth largest world producer behind only Nigeria, Thailand and Indonesia.

Cassava plays an important role in the social and economic spheres in family farming. The agricultural product is often the main crop produced by certain regions. Thus, many families work in the cultivation, processing and commercialization of the generated cassava products. The roots are usually processed in industries with little technology, giving rise to by-products.

In the production of flour, are generated two types of wastewater, the first type is derived from the water used to wash the roots, and the second is the liquid extracted from the roots during pressing [11] which is commonly called "*Manipueira*" in

Fig. 1 Cassava wastewater storage tank

Brazil, a yellowish liquid with a high concentration of organic matter, nutrients and hydrocyanic acid. In the production of flour, the effluent (*Manipueira*) is disposed of separately immediately after pressing, while in the production of starch, it is mixed with the high volume of drinking water used in the various stages of crushing, sieving and sedimentation. Because of this, the volume of wastewater generated in the starch production process is higher than that verified in the production of flour.

The estimated generation of *Manipueira* in flour houses is about 300–600 L for each ton of processed cassava roots [12, 13]. Meanwhile, in the starch factories, which have high technology, according to the literature, 2.75–6.3 m^3 of cassava wastewater (*Manipueira* and water) are generated for each ton of roots processed [14, 15]. According to the Food and Agriculture Organization of the United Station [11], this volume may be even higher, depending on the process used and the country, the amount of wastewater per ton of roots processed in the starch industries can reach up to 18 m^3.

In Brazil, most of the cassava production is for the manufacture of flour. The estimate is that the product consumes 60–80% of the total production of cassava roots [16–18]. Trying to provide more alternatives for the destination of the generated effluent, in this book, were conducted several kinds of researches with the use of *Manipueira* from flour houses.

From now on, whenever the term “cassava wastewater” is mentioned in this book, it is understood that it is the “*Manipueira*” extracted in the production of flour. Figure 1 shows the cassava wastewater stored in a tank right after processing cassava in a flour mill.

Madeira et al. [19] claim that the toxicity of this effluent represents a major environmental problem, as it is usually not treated before being discarded. When it is considered the processing of 70% on the average Brazilian production of 22.5 million tons/year and a generation of 300 L per ton of cassava wastewater, in the flour production, approximately 4.73 billion liters of the effluent are generated annually just in Brazil. This fact demonstrates a need for alternatives for the correct destination

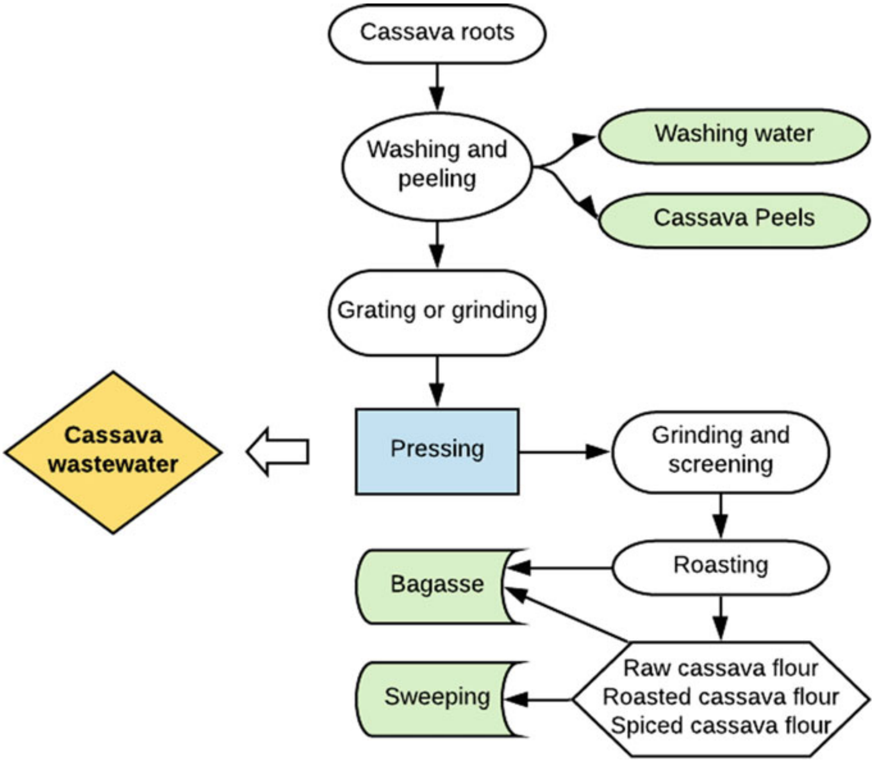

Fig. 2 Steps of the cassava flour manufacturing process

of this waste. A flowchart in Fig. 2 shows the origin of the cassava wastewater from processing the roots in a flour mill.

The cassava wastewater composition is variable as it depends on the crop and on typical characteristics of the region where the cassava is grown, such as the type of soil and the climatic factors. Table 1 below shows the results of the chemical composition of the cassava wastewater used in the studies presented in this book.

The results obtained for the cassava wastewater characterized in this work show high potassium, nitrogen, sodium, iron and calcium concentrations, which is in accordance with the values found in the literature by Silva et al. [20]. The variations of the values obtained in comparison with the literature can be justified by the fact that the composition changes according to several factors such as climate, soil, crop, among others. The low pH presented demonstrates the acidity of the wastewater, and a high value of solids present in the liquid can also be observed, showing the presence of organic matter. The high values of chemical oxygen demand (COD), 14.70–101.38 gO2/L, and biological oxygen demand (BOD), 6.21–29.20 gO2/L, presented in the literature, express the high organic load of cassava wastewater and show that the effluent is a source of pollution [20, 21].

Table 1 Chemical composition of cassava wastewater

Parameters analyzed	Values
Nitrogen (mg/L)	1121
Phosphorus (mg/L)	132
Potassium (mg/L)	1456
Calcium (mg/L)	93
Magnesium (mg/L)	219
Sodium (mg/L)	351
Zinc (mg/L)	20
Copper (mg/L)	9
Iron (mg/L)	117
Manganese (mg/L)	15
Total solids (g/L)	14.56
Suspended solids (g/L)	2.37
Chloride (mg/L)	545.40
Sulfur (mg/L)	78.53
Phosphate (mg/L)	27.07
Cyanide (mg/L)	5.62
pH	4.5

Table 2 Chemical composition of cassava wastewater powder

Oxide	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	SO_3	P_2O_5	Na_2O	Br
Weight (%)	2.457	2.306	15.922	32.654	25.739	3.123	3.592	9.986	4.220

Was performed an X-ray fluorescence (XRF) assay to determine the oxides present in the waste. The settleable solids present in the liquid were used in the test. The material was dried in an oven at a temperature of 60 °C for 24 h to obtain the powdered cassava wastewater. Table 2 shows the results obtained in the XRF assay. The results demonstrate that the significant potassium (K_2O), calcium (CaO), iron (Fe_2O_3) and sodium (Na_2O) levels are similar to the results presented in the reference tests performed on the liquid, as shown in Table 1.

The cassava wastewater has high levels of solute, including starch made up of polymeric molecules which have binding properties acting as a biopolymer. Starch molecules together with solids in solution can improve the plasticity of the mixture and its resistance by filling empty spaces and their effect as a binder. The plasticizer characteristic can be seen in the study by Akindahunsi and Schmidt [22], who studied the effect of cassava starch on the contraction properties of concrete. They obtained a decrease in shrinkage with the increase in the use of cassava starch by up to 2% by mass. Abd et al. [23] studied the effect of using corn starch in a concrete mixture, obtaining an improvement in workability with an increase in density and resistance to compression with the use of 1% corn starch.

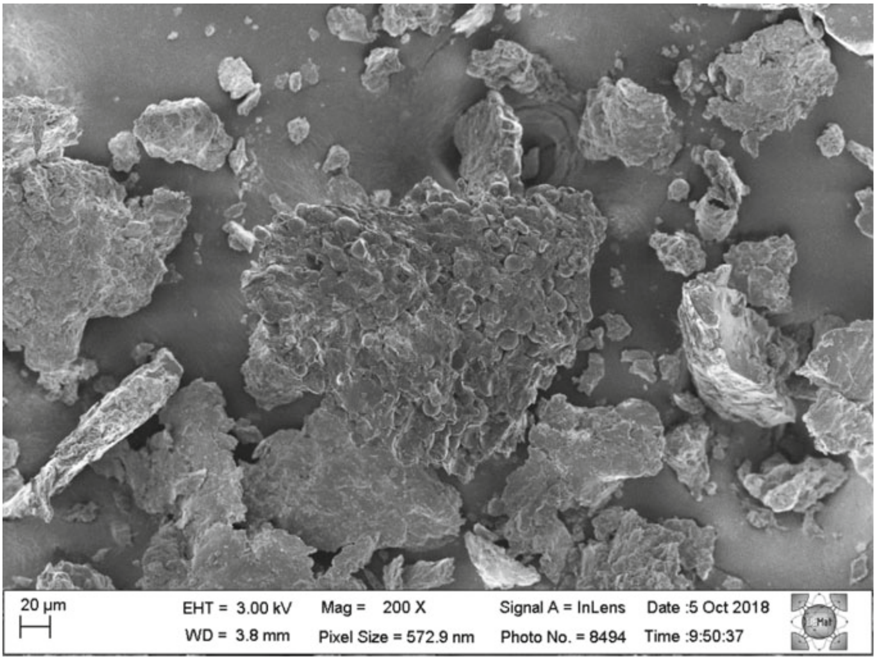

Fig. 3 SEM of cassava wastewater powder sample 200× magnification

The starch particles from the cassava starch are predominantly oval or spherical. There is also a difference in the granule size ranging from 4 to 15 μm, with an average of 10 μm for the cassava granules [24].

The powder was subjected to the scanning electron microscopy (SEM) test to observe the morphology of the solid part of cassava wastewater. The starch globules clustered can be seen in Fig. 3.

In Fig. 4, it is possible to observe oval starch globules with sizes around 10–14 μm. The globes have shapes and sizes similar to those found by Vieira et al. [24].

In relation to cyanide, there is an important concern on the part of Occupational Health agencies with the control and exposure of workers to chemical agents. The Occupational Safety and Health Administration [25] establishes a maximum occupational exposure limit to hydrocyanic acid of 10 parts per million (ppm) in an 8-h workload per day. However, the regulatory standard NR 15 [26] establishes a tolerance limit of 8 ppm for the same 8 h. Thus, cassava wastewater must be placed in an environment which allows ventilation for 48 h in order to reduce the cyanide content present in the composition and be exposed to the sun so that the hydrocyanic acid (HCN) (which has a boiling temperature of 25.6 °C) volatilizes. According to Tokarnia et al. [27] and Silva [28], cassava wastewater has its cyanide content reduced to half in 24 h by this procedure, and it further decays to less than 1/4 with 48 h. The hydrocyanic acid content shown in Table 1 was well below that found by Silva et al. [20] and Peres et al. [21], and this is due to the fact that the cassava wastewater was