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(RESEARCH ARTICLE)



Extraction of raw potash from cocoa pods: Influence of time and water volume

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Abstract

This paper has been written as part of recovery of cocoa waste. This study aims to extract raw potash from the ashes of dry cocoa pods using distilled water. For this purpose, cocoa pods and distilled water have been used. Two methods have been conducted: In the first part, a 50-gram sample of ash is dissolved in different volumes of distilled water that are 100, 200, 300, 400, 500 and 600 ml and then left to stand for 24 hours. In the second part, 50 g of ash are dissolved in 200 ml of distilled water with variable contact times between water and ash ranging from 1 hour to 8 hours, in one-hour steps. The filtrates obtained from solution are heated to evaporation in an oven to recover the pellets and weighed. Results shows that the masses of raw potash collected increase with the volume of the water, alsothe masses of raw potash pelletsincrease with the duration of the water-ash contact.

Keywords: Cocoa Waste; Cocoa Pods; Ashes; Raw Potash Pellets

1. Introduction

With the consideration of the concepts of sustainable development and circular economy, the valorization of agricultural by-products is gaining momentum in certain countries whose economy is based on agriculture such as Ivory Coast. Indeed, Ivory Coast, the world's leading cocoa producer, by-products from these industrial products are used as fertilizers for soil fertilization, (Konan, 2019), (Adom *and* Yao, 2020), (Kouassi *and* Tano, 2021). Similarly, other studies have endeavored to use ash from agricultural by-products as cement additives. Rice husk ash has a high amorphous silica content (Mehta, 1987). They react with the free lime in cement to produce calcium silicate hydrates which increase the compressive strength of concrete. The addition of 10 to 20% of rice husk ash to cement improves the durability of concrete to attacks by chloride and sulfate ions (Ganesan *et al.*, 2008). Sugarcane stalk ash has an interesting pozzolanic effect (Khalil *and* Anwar, 2015). Walnut shell ash has similar characteristics to sugarcane stalk ash if made finer, but it contains less silica. Calcined biomass ash contains minerals: silica and calcium, which are involved in pozzolanic reactions. In addition, the work carried out by Akon *et al.*, 2024 has shown the pozzolanic potential of palm kernel waste ash as a cementitious additive; this ash has very interesting pozzolanic properties and can be used in cementitious materials.

According to ASTM C 618 standards, ash is classified into three classes (F, C and N). Among these, class N ash is numerous but has low reactivity. However, some contain high proportions of potash. Recent studies indicate that potash can be used to produce geopolymers. Geopolymers are mineral materials obtained by polymerization of aluminosilicates (clays, slags etc.) activated by an alkaline solution such as potash to create a stable three-dimensional structure. Thus, the potash contained in the ash from agricultural by-products could be extracted and used in the manufacture of geopolymers usable in construction. This extraction of potash from agricultural by-product ash would not only be a solution to reduce the carbon footprint linked to the production of Portland cement, but would also

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contribute to the circular economy by giving value to unused resources while reducing the environmental impact of the construction industry. Cocoa pods are a source for the production of potash from biomass. However, is it advisable to optimize potash production from these ashes?

To address this issue, techniques such as acid leaching, alkaline hydrolysis, and enzymatic biodigestion for the extraction of minerals from agricultural residues are distinguished by their efficiency and low ecological impact (N'guessan *et al.*, 2021). For example, acid leaching can extract minerals from cocoa shells, while alkaline hydrolysis can efficiently recover phosphates from plant waste (Koffi *and* Kouamé, 2018). Similarly, the use of specific enzymes in the biodigestion of corn residues significantly improves the availability of potassium and organic nitrogen (Fofana *and* Diallo, 2023). The implementation of some of them is quite complex. Also, to allow the popularization of geopolymers from potash extracted from biomass, the leaching technique was used in this study. The aim of this study is to define the optimal conditions for the leaching of potash from cocoa pod ash. This involves determining the influence of solvent volume and treatment duration on the quantity, purity, and kinetics of potash pellet production. Understanding the influence of these production conditions will help improve potash extraction from potash-rich ash.

2. Methodology

2.1. Material

2.1.1. Dried cocoa pods

The dried pods of cocoa (Theobroma cacao) used in this study come from the town of Fresco, located 176 km as the crow flies from Abidjan. After collection, they are stacked and dried again. They are then carefully cleaned to remove any sand and other debris. These dried pods are calcined, and the resulting ash is passed through a 125-micrometer sieve. This sieve is used for the rest of the work.

2.2. Methods

The experimental method is carried out in two stages. In the first part, a 50-gram sample of ash is dissolved in different volumes of distilled water and then left to stand for 24 hours. The first volume of water is 100 ml. To obtain the other volumes, the quantity of water is increased by 100 ml until reaching 600 ml. After 24 hours of contact between the ash and the water (Figure 1), the solution is filtered and then the filtrate (Figure 2) is heated in an oven at 105° C until pellets appear.

In the second part, 50 g of ash are dissolved in 200 ml of distilled water with variable contact times between water and ash ranging from 1 hour to 8 hours, in one-hour steps. The solutions obtained are filtered, and the filtrates are heated in an oven to recover the pellets. Each mass of pellets and the ash are weighed (Figure 3).





Figure 1 Ash-water mixture

Figure 2 Filtrate



Figure 3 Collected pellets of potash

Table 1 Summary of the experimental protocol

Ash mass (g)	Contact duration (Hours)	Volume of distilled water used (ml)	Solution ID
50	1	200	S 200-1
50	2	200	S 200-2
50	4	200	S 200-4
50	6	200	S 200-6
50	7	200	S 200-7
50	8	200	S 200-8
50	10	200	S 200-10
50	12	200	S 200-12
50	24	200	S 200-24
50	24	100	S 100-24
50	24	300	S 300-24
50	24	400	S 400-24
50	24	500	S 500-24
50	24	600	S 600-24

3. Results

3.1. Influence of solvent volume on ash dissolution

The results of the variation of the masses of potash collected as a function of the volume of solvent are presented in Figure 4.

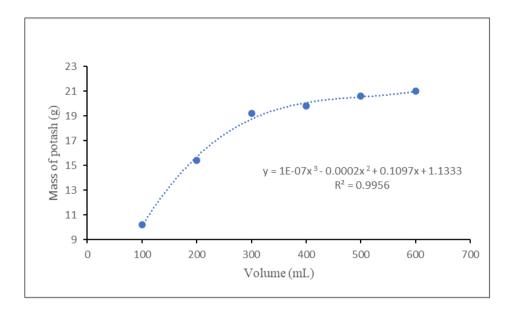


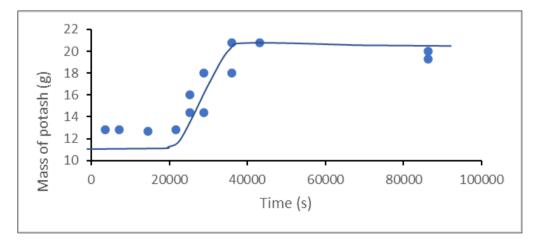
Figure 4 Evolution of the mass of crude potash as a function of the volume of the solvent

This figure shows that the masses of raw potash collected increase with the volume of the solvent. For example, when the solvent is 100 ml, the mass of raw potash collected is 10.2 g. This mass increases from 19.2 g when the solvent volume increases to 300 ml. This corresponds to an increase in the mass of raw potash of 88% compared to the solvent volume of 100 ml. The increase in the volume of solvent in the cocoa pod ash (ash/solvent ratio \geq 1/6) promotes a strong release of potash into the solution.

MK
$$\xrightarrow{\text{H}_2\text{O}}$$
 $\text{K}^+ + \text{M}^ \xrightarrow{\text{filtration} \text{and the}}$ KOH (After filtration and the heating)

Figure 4 also shows that when the solvent volume is greater than or equal to 400 ml, i.e. an ash/solvent ratio $\leq 1/8$, the rate of increase in potash release is 0.6%. This decrease in the potash dissolution rate with an increase in the quantity of solvent is explained by the low proportion of potash still present in the ash suspended in the mixture. This dissolution reaction can be written:

3.2. Influence of the duration of solvent-ash contact on ash dissolution



 $\textbf{Figure 5} \ \, \textbf{Evolution of the mass of potash extracted as a function of the time of water-ash contact}$

Figure 5 describes the variation of the masses of raw potash collected for a ratio of mass of ash to mass of solvent equal to $\frac{1}{4}$ as a function of time. This figure shows that the masses of raw potash vary with the duration of the water-ash contact. From 0 to 21600 s or 6 hours the mass of potash collected is practically constant, approximately 12.8 g. From 21600 s to 36000 s or 10 hours, the mass of potash recovered increases from 12.8 g to 20.6 g, then beyond 6 hours it becomes constant again and stabilizes around 20.6 g.

4. Discussion

The extraction of potash from cocoa pod ash is influenced by the amount of solvent (water) used. It increases with the amount of solvent to reach an equilibrium when the mass ratio of ash to mass of solvent is less than 1/8. Similar results have been obtained by some authors who have worked on the dissolution or extraction of minerals from ash. According to Stumm and Morgan, (1996) adding a larger volume of water reduces the concentration of dissolved ions in the solution, thus promoting the dissolution of new constituents of the ash according to Le Chatelier's law (Le Chatelier, 1884;). Indeed, an unsaturated solution will allow more minerals to pass into solution until a new equilibrium is reached Baes and Mesmer (1976). Similarly, in their work, Evangelou, (1998) and Sparks, (2003) showed that increasing the volume of water slows down the reaching of saturation, thus prolonging the dissolution process of the minerals present in the ash. This is particularly important for soluble elements such as potassium, sodium, carbonates and sulfates, which are often present in significant quantities in plant ash. (Rodier et al., 2009).

The variation in mass as a function of contact time could be explained by several physicochemical mechanisms involved in the dynamics of dissolution and diffusion of minerals contained in the ash. In the first few seconds, soluble minerals easily accessible on the surface of the ash particles dissolve rapidly. However, the process quickly reaches a temporary equilibrium, because the internal particles are not yet reached by water: this is the initial dissolution (Stumm and Morgan 1996). Then the increase in the mass of crude potash could be due to the slower and longer dissolution of minerals strongly bound to the ash particles, whose dissolution requires particular chemical conditions. The last plateau corresponds to the establishment of a new equilibrium or the unavailability of minerals, because beyond a certain duration of ash-water contact, the quantity of minerals extracted with the variation of time becomes zero, this would indicate that all soluble minerals have been dissolved and that a new equilibrium would be reached. This level can also be explained by the more or less total dissolution of the potash contained in the ash.

For efficient water extraction of potash from cocoa pod ash, the ash must be left in contact with water for at least 10 hours. During this extraction, the raw pellets obtained are a mixture of potash and other minerals contained in the ash. It is therefore important to determine the purity level of this raw potash.

5. Conclusion

This study provided a demonstration of variation of raw potash pellets mass extracted from cocoa ashes with these two methods. The increase in water in the ash gradually increases the quantity of raw potash, as does the increase in the contact time of the mixture between water and ash. Cocoa pod ash is an excellent source of potash.

Compliance with ethical standards

Disclosure of conflict of interest

Noconflict-of-interestto be disclosed.

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