KINETICS STUDY OF Si RELEASE FROM SILICA SYNTHESIZED FROM SUGARCANE WASTE ASH

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ABSTRACT

Sugarcane bottom ash (SWA) is a byproduct generated in substantial quantities globally, creating significant environmental challenges due to inadequate disposal practices. This study focused on the extraction of high-purity silica from SWA using the sol-gel method, a process known for its efficiency in producing high-quality materials. Advanced characterization techniques, including X-ray fluorescence (XRF) and X-ray diffraction (XRD), confirmed the successful production of amorphous silica with a purity of 98%, demonstrating the effectiveness of this method. To further evaluate the Si content, the synthesized product underwent chemical treatment using a combination of citric acid, hydrochloric acid, and a salt mixture for a period of 48 h. This critical step improved the properties of the material and prepared it for further analysis. Kinetic parameters were determined to characterize the silicon release behavior under various conditions, providing valuable information on the potential of the material as a slow-release fertilizer. Four mathematical models—first-order equation, power function, parabolic diffusion, and Elovich model—were employed to describe the kinetics of Si release, providing insights into the product's agricultural applications. The findings suggest that silica synthesized from SWA is not only a sustainable alternative to conventional fertilizers but also supports circular economy principles by transforming waste into valuable resources. Furthermore, this innovation aligns with the Sustainable Development Goals (SDGs) related to responsible consumption, production, and sustainable agriculture. By addressing environmental and agricultural challenges, this research highlights the dual benefits of waste management and resource efficiency. It demonstrates the role of innovative waste valorization strategies in promoting sustainability across industries and unlocking broader applications in the environmental and agricultural sectors, ultimately demonstrating the potential of SWA as a key resource in sustainable development.
Keywords: agricultural waste; slow-release fertilizer; sustainable agriculture; circular economy; sol-gel method.

1 INTRODUCION

Sugarcane waste ash is a residue generated in large quantities and can be utilized as a raw material for the production of silica nanoparticles (SiNPs) through the sol-gel method (Rovani *et al*., 2018; 2019; Alves *et al.*, 2017). The high Si content of SiNPs has led to interest in its use as a source of silicon for plants.

Silicon (Si), a beneficial element for plants, is known in alleviating biotic and abiotic stresses in plants (Luyckx *et al*, 2017). The evaluation of silicon available in fertilizers and soil amendments can be performed in the laboratory by the extraction method. The extraction method consists of a test in which a liquid extractant (water, acid, saline solution, etc.) is placed in contact with the fertilizer for a certain time. Afterwards, the amount of silicon present in the extract is determined.

The purpose of an extractor is to resemble as closely as possible the ability of plant roots to absorb nutrients available in the soil, i.e., it must solubilize the amount of nutrients that would be available in the soil solution for plants to absorb (Assis, 2011; Buck; Korndörfer; Datnoff, 2010; Buck, 2010; Pereira *et al*., 2003).

The objective of this study was to evaluate the release of silicon from a sample of silica synthesized from sugarcane residues using the results obtained through the extraction methodology.

2 MATERIALS AND METHODS

All reagents used were analytical. The sugarcane waste ash was provided by sugar-alcohol plant located in Lins (SP-Brazil). Oven (Fanen Orion model 515), muffle furnace (Quimis - model Q-318M24) and reflux system were used. Silicon concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES Spectrometer – BRAND SPECTRO ARCOS).

2.1 Synthesis of silica from sugarcane waste ash

The synthesis process involves three steps. First step: homogeneous mixture of the ash with NaOH in the ratio 1:1.5 (% mass) was placed in a muffle furnace at 450 °C for 1 h. In step 2, after complete cooling at room temperature, water was added to the molten mixture at the rate of 8 mL per gram of ash and the suspension was placed under reflux for 1 h. The suspension was then filtered to separate the residue from the sodium silicate solution. In step 3, 6 mol L^{-1} H_2SO_4 was slowly added in the sodium silicate solution with constant agitation, so that the pH decreased to 4. Then, the suspension was filtered, the silica sample was washed to remove the salt formed during the precipitation stage, and dried in an oven at 120 °C for 12 h. The characterizations were performed by XRD (Rigaku Multiflex diffractometer) and XRF (Zetium X-ray fluorescence spectrometer, Pananalytical).

2.2 Determination of Si content as a function of time

Samples of 0.4 g of silica were placed with the following aqueous solutions: 60 mL of 0.5 mol L^{-1} HCl; 30 mL of Na_2CO_3 10 g L^{-1} with 30 mL of NH_4NO_3 16 g L^{-}1 (salt mixture); 60 mL of 0.1 mol L^{-1} citric acid. The samples were kept at rest for 3, 6, 12, 24, 36 and 48 h. After each resting time, the samples were filtered. Silicon concentrations in the filtered solutions were determined. All release tests were performed in triplicate. The kinetic equations used to describe the rate of Si release were first-order equation, power function, parabolic diffusion and Elovich (França *et al*., 2017; Yongling; Cheng, 2016; Jalali; Zarabi, 2006; Shariatmadari; Shirvani; Jafari, 2006; Jiang yi-chao, 2004 *et al*., 2004; Sparks; Carski, 1985).

3 RESULTS AND DISCUSSION:

3.1 Characterization of sugarcane waste ash

The chemical composition of sugarcane waste ash (SWA) is shown in Table 1. The major component was SiO_2 content with 90 wt%., indicating that this material is suitable to use as a source of silica for producing sodium silicate solution. The second component in greater quantity is potassium and the other oxides were considered impurities because they have a content < 0.80%. Sugarcane residue ashes generated in sugar-alcohol plant located in different regions of Brazil showed SiO_2 content between 61.0 and 96.2% (Alves *et al.*, 2017; Almeida *et*

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al., 2015; Faria; Gurgel; Holanda, 2012; Sales and Lima, 2010). The SWA diffractogram (Figure 1) indicated the only presence of quartz in the crystalline phase (SiO_2, ICDD01- 085-0794). The crystalline phase of silica in quartz form is related to the conditions of combustion of sugarcane waste at temperature higher than 900 °C (Le Blond *et al.*, 2010).

Table 1. Chemical composition of sugarcane waste ash and synthesized silica

Oxides	SWA (wt%)	Silica (wt%)
SiO_2	90.2	97.714
K_2O	2.00	0.086
SO_3	0.32	1.712
Fe_2O_3	0.88	0.343
MgO	0.81	0.018

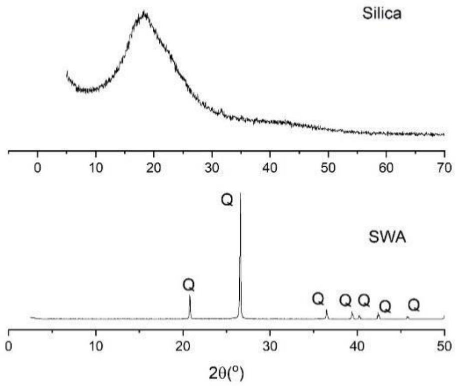

Figure 1. X-ray diffractograms of the sugarcane waste ash (SWA) and synthesized silica

3.2 Characterization of silica Gel

The oxide compositions of produced biosilica from XRF are shown in Table 1. It was possible to observe a significant increase in the purity of the material where a Si content of 90.2 wt.% for sugarcane waste ash increased to 97.7 wt.% for the silica. These results demonstrate a significant purification of sample that generates high pure silica gel. Generally. the sol–gel method resulted in purity ranged from 93 to 99 wt.% (Rovani *et al*., 2023; Alves *et al.*, 2017). The diffractogram of synthesized silica indicate the presence of amorphous silica only which is characterized by the presence of a broad single peak, reaching its maximum at θ=22° (Figure 1). It is also possible to observe the absence of impurities, such as Na_2SO_4, or crystalline unreacted silica.

3.3. Determination of Si content as a function of time

Figure 2 shows the content of solubilized Si in the liquid extracts as a function of time. The Si release curve in aqueous solution of salt mixture showed the sigmoidal format, which is considered ideal for a slow-release fertilizer. In citric acid and hydrochloric acid solutions, the Si release content was approximately equal. The increase in release was gradual and has not reached a threshold until 48 h of contact.

The release of Si was at least 10 times higher in the salt mixture than in the acid extractors. This fact is because the salt mixture solution is alkaline (pH 9) and OH^- ion acts as a catalyst to form monosilicic acid during the dissolution of silica. Monosilicic acid is the form absorbed by plants. Also, NH_4^+ is a source of protons that aids the formation of monosilicic acid (Bernauer *et al.*, 2019; Pereira *et al.*, 2003).

The kinetic data for Si release are shown in Table 2. The best models for describing the Si release kinetics were: first-orde for salt mixture, parabolic diffusion for citric acid and power function for hydrochloric acid .

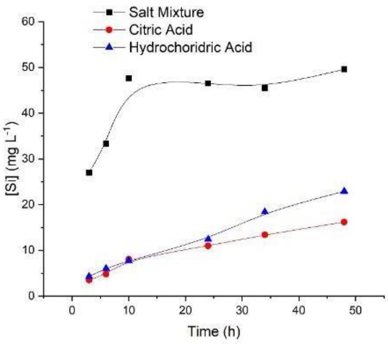

Figure 2. Release curves for Si using extracts solutions

Table 2. Kinetic models of Si release from synthesized silica

Kinetic Models	Salt mixture	Citric Acid	Hydrochloric Acid
First-order equation			
a (mg L^{-1})	47.6	16.2	31.2
b (h^{-1})	0.254	0.0582	0.0261
R^2_{aj}	0.8768	0.9556	0.9485
Power function			
a (mg L^{-1} h^{-b})	25.9	2.09	1.65
b (sem dimensão)	0.175	0.528	0.676
R^2_{aj}	0.6673	0.9860	0.9804
Parabolic diffusion			
a	26.4	-0.552	-2.92
b (mg L^{-1})$^{-0.5}$	3.65	2.41	3.57
R^2_{aj}	0.5721	0.9867	0.9652
Elovich			
a (mg L^{-1} h^{-1})	137.9	1.35	0.980
b (L mg^{-1})	0.133	0.152	0.0613
R^2_{aj}	0.7150	0.9831	0.9595

4 CONCLUSION

This study demonstrate the potential of sugarcane waste ash (SWA) as a raw material to synthesize a Si slow-release fertilizer. The sol-gel process used to extract the silica from

SWA was able to precipitate more 97% of amorphous silica. The essays of Si release from the silica using salt mixtures, citric acid and hydrochloric acid solutions showed the small solubility of the synthesized silica. The release of Si was at least 10 times higher in the salt mixture than in the acid extractors. The Si release profile was analyzed using different kinetic models. The utilization of silica-based on agricultural waste as slow-release fertilizer contributes to achieve multiple UN SDGs, particularly those related to SDG 2 and 12.

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