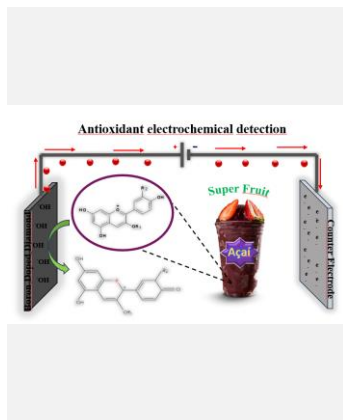


Electrochemical technologies as an Innovative Approaches for valorizing Açai (*Euterpe Oleracea*) determination of the Antioxidant Capacity

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Electrochemical technologies has the potential to both reduce the environmental impact of the effluent and provide economic opportunities by identifying/recovering valuable compounds and clean water. Therefore, electrochemical assays were used to determine the total antioxidant capacity of frozen açai pulp, a fruit mainly known for its high nutritional value, as an innovative approach for valorizing compounds. The ethanolic extract obtained by a nonconventional ultrasound bath showed a redox behavior at +0.37 V and +0.27 V (vs. Ag/AgCl) for the anodic and cathodic peak respectively, when evaluated by cyclic voltammetry and, differential pulse voltammetry profile at different supporting electrolytes with an ethanolic antioxidant extract indicated the importance of maintaining a pH with a buffer when measuring an antioxidant as it lowers the detection limit. By establishing the correct scan rate, supporting electrolyte, and working electrode, it was determined that the frozen açai pulp extract has a total antioxidant capacity of $4.91 \mu\text{A V}^{-1}$.

Introduction

Açai is a berry fruit known as a superfood due to the high antioxidant content, which provides beneficial properties when consumed. This property has attracted the attention of the Brazilian population, who usually consume it in form of juice, energy drinks, açai bowls, and ice-cream among others. Approximately 1.7 million tons of açai were recollected in 2022 of which 8200 tons were destined for exportation and the rest for local consumption [1]. During this industrial process, significant amounts of commercial products and residues are produced. Then, in both cases, the identification of new chemical features and applications of açai as well as the recovery of nutrients from wastewater and its valorization, are promising approaches to promote the transition of current economy into a circular economy.

Rapid, easy, and sensitive methods are available from the field of electroanalytical chemistry for determining the redox properties and antioxidant activity of relevant substances in a wide range of samples [2]. This can be an innovative alternative to valorize starting materials or residues. Considering electroanalysis as an innovative and rapid method, it holds certain advantages over traditional optical methods; for instance, it can be selective depending on the electrode used, it has low detection limits, thereby not requiring much sample; and no hazardous reagents are employed [2], [3].

This fact leads us to investigate the feasibility of determining the antioxidant capacity by electrochemical methods, comparing two working

electrodes, glassy carbon (GCE) and boron doped diamond electrode (BDDE) in different supporting electrolytes (phosphate buffer solution (PBS), sodium chloride and sodium nitrate).

Material and Methods

Açai extract was obtained by a non-conventional technique of an ultrasound bath of frozen açai pulp with ethanol 99%, centrifuged at 1000 rpm for 10 minutes and then filtered. The supernatant was placed with the supporting electrolyte in a three-electrode cell of 25 mL to perform cyclic and differential pulse voltammeteries using a potentiostat/galvanostat. GCE and BDDE were used as working electrodes, while Ag/AgCl and platinum were the reference and auxiliary electrodes, respectively.

Results and Discussion

The results obtained with GCE related to the effect of the scan rate in presence of the antioxidant extract (AE) in phosphate buffer solution at pH 5 with NaCl as supporting electrolyte are shown in Figure 1. The observed potential peak at +0.37 V (vs. Ag/AgCl) is the signal obtained of the simultaneous oxidation reaction of water and açai antioxidant on the GCE's surface. Furthermore, a reduction potential peak is also observed at +0.27 V (vs. Ag/AgCl), indicating a reversibility behavior of the antioxidants present in the sample.

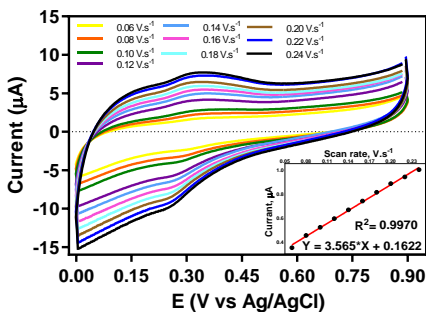


Figure 1. Cyclic voltammograms of açai pulp extract 0.2% with GCE at different scan rates (60 – 240 mV s^{-1}) in (A) PBS and (B) PBS with NaCl. The inset plots correlate the peak current as function of the scan rate.

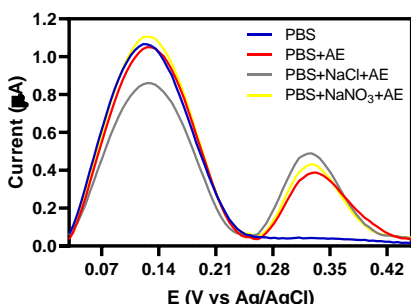


Figure 2. Differential pulse voltammograms of GCE in phosphate buffer solution (0.1 M) pH 5 with açai pulp extract (0.2%) at scan rate 0.1 V s^{-1} in different supporting electrolytes.

According to the literature, the sum of the ratios between the anodic peak current and the anodic peak potential serves to determine the total antioxidant capacity by means of the electrochemical

Conclusions

It was possible to observe the presence of antioxidants in a sample of frozen açai pulp detected at the GCE and it was quantified using the EI to obtain the total antioxidant capacity; however, no effect was observed from the analysis on BDDE. Furthermore, it should be expected to be reproducible and feasible for antioxidant capacity determinations in plant matrices by using GCE in PBS at pH 5 and NaCl as supporting electrolyte. This study confirms the strong antioxidant capacity of açai pulp and the rapid antioxidant detection by electrochemical assays is an excellent alternative for valorization of residuals.

Acknowledgments

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index (EI), thus being $4.91 \mu\text{A V}^{-1}$ for the ethanolic extract of frozen açai pulp 0.2%. As it is a commercial pulp, a lower antioxidant capacity than those reported in the literature for powdered samples was expected [2]. The behavior of the extract was evaluated by using differential pulse voltammetry comparing the use of NaCl, NaNO_3 and PBS as supporting electrolytes at GCE (Figure 2). The first anodic peak at +0.12 V (vs. Ag/AgCl) for all the supporting electrolytes can be attributed to the natural behavior of our system due to the presence of that peak in absence of the AE. Nevertheless, oxidation peaks at +0.33, +0.32 and +0.34 V (vs. Ag/AgCl) for PBS, PBS with NaNO_3 and PBS with NaCl, respectively, can be attributed to the antioxidants present in the sample.

Meanwhile, BDDE showed an inverse effect when different concentrations of açai extract are present in PBS with NaCl (Figure 3). The anodic current peak decreased as the extract concentration increased, similar to what occurs at an electrode's surface when it has been compromised with a passivating polymeric film [4].

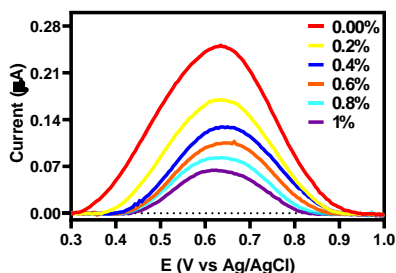


Figure 3. Differential pulse voltammograms of BDDE in PBS (0.1 M) pH 5 with NaCl and different açai pulp extract concentrations between 0.2 to 1.0% at scan rate 0.1 V s^{-1} .