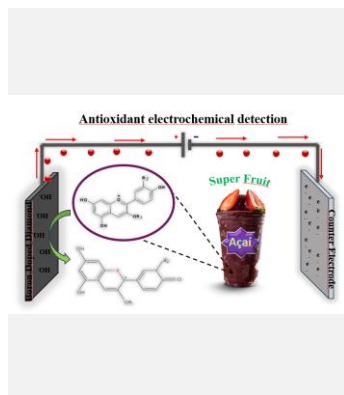


Electrochemical Determination of the Antioxidant Capacity of Açai (*Euterpe Oleracea*) as an Innovative Approach

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Electrochemical assays were used to determine the total antioxidant capacity of frozen açai pulp, a fruit mainly known for its high nutritional value. 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 of the 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 $4.91 \mu\text{A}\cdot\text{V}^{-1}$.

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]. There are multiple methods to determine the total antioxidant capacity; however, it is safe to say that by defining their potential to oxidize reactive oxygen or nitrogen species with an electrochemical assay, we can justify the fruits antioxidant capacity, as well as understanding the action of the bioactive compounds and the redox behavior [2]. 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, in addition to comparing two working electrodes, glassy carbon (GCE) and boron doped diamond electrode (BDDE), frequently used in electroanalysis and, to understand the effect of 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. Glassy carbon and boron doped diamond electrode were used as working electrodes, while Ag/AgCl and platinum were the reference and auxiliary electrodes, respectively.

Results and Discussion

The results obtained with glassy carbon electrode of 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 is shown in Figure 1.

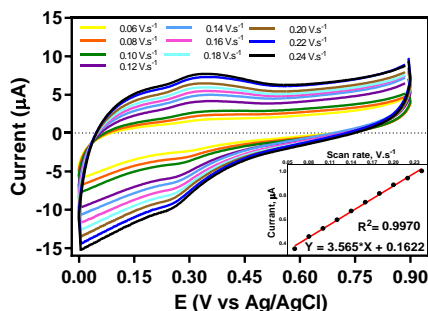


Figure 1. Cyclic voltammograms of açai pulp extract 0.2% with GCE at different scan rates (60 – 240 $\text{mV}\cdot\text{s}^{-1}$) in (A) PBS and (B) PBS with NaCl. The inset plots correlate the peak current as function of the scan rate.

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.

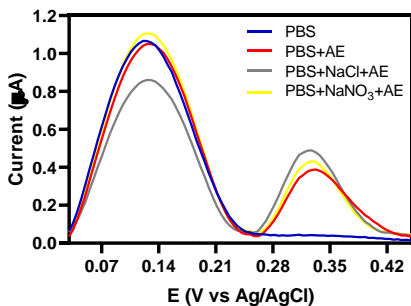


Figure 2. Differential pulse voltammograms of glassy carbon electrode in phosphate buffer solution (0.1 M) pH 5 with açai pulp extract (0.2 %) at scan rate 0.1 V s⁻¹ in different supporting electrolytes.

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 index (EI), thus being 4.91 µA.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].

Conclusions

It was possible to observe the presence of antioxidants in a sample of frozen açai pulp detected at the glassy carbon electrode and quantified using the electrochemical index to obtain the total antioxidant capacity; however, no effect was observed from the analysis on the boron doped diamond electrode. Furthermore, by using glassy carbon electrode in PBS at pH 5 and NaCl as supporting electrolyte should be expected to be reproducible and feasible for antioxidant capacity determinations in plant matrices. This study confirms the strong antioxidant capacity of açai pulp and the rapid antioxidant detection by electrochemical assays. In addition to the time relevance, electroanalysis showed to be sensitive methods with low detection limits.

Acknowledgments

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The behavior of the extract was evaluated by using differential pulse voltammetry comparing the use of NaCl, NaNO₃ and PBS as supporting electrolytes with a glassy carbon electrode (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 NaNO₃ and PBS with NaCl respectively, can be attributed to the antioxidants present in the sample.

Boron doped diamond electrode showed an inverse effect when adding different concentrations of açai extract 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].

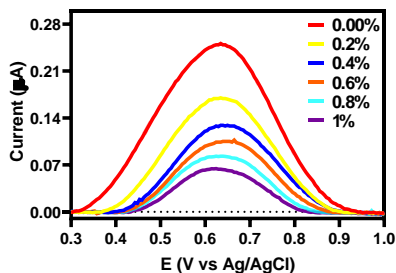


Figure 3. Differential pulse voltammograms of BDDE in PBS (0.1 M) pH 5 with NaCl and different açai pulp extract concentrations between 0.2 to 1.0 % at scan rate 0.1 V s⁻¹.

