NEW METHODS FOR DETERMINATION OF CARBOXYLIC ACIDS, AMINO ACIDS AND POLYOLS IN VINASSE OF THE MANUFACTURING PROCESS OF ETANOL

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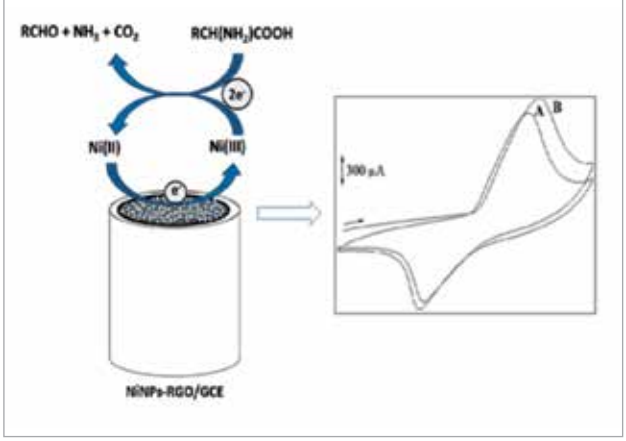

Figure 1. Modified electrode with graphene oxide containing nickel nanoparticles for determination of amino acids. Cyclic voltammograms at NiNPs-RGO/GCE in 0.1 mol L^{-1} NaOH solutions (A) in the presence of 1.0 mmol L^{-1} Alanine (B)

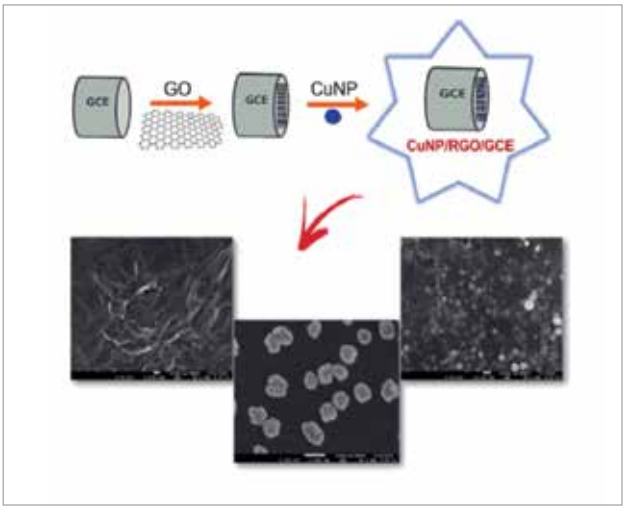

Figure 2. Modified electrode with graphene oxide containing copper nanoparticles for determination of polyols

The full energy utilization of sugar cane should be linked with the current biorefinery concept, which allows the conversion of biomass, besides the production of sugar and ethanol in various chemical products with high added value. Sugar and ethanol plants have on their plants, two residues (bagasse and vinasse) that can generate products with high added value. These wastes, bagasse has been used in the production of electricity and recent research shows its viability in the production of second generation ethanol. However, vinasse until now, has been used only as fertilizers in their own plantations cane sugar. Vinasse is a product of the distillation of ethanol being produced in a proportion which may range 11 to 18 liters per liter of distilled alcohol. This residue, consisting mainly of polyols, carboxylic acids and amino acids in significant concentrations, has attracted little attention as meaning transform vinasse as a significant industrial importance. The development of new methods for the determination of compounds with high added value is essential for the sugarcane mills can reclaim what is now considered waste. Among these new methods of determination, those using electrochemical sensors and electrochemical detectors coupled with separation techniques has distinguished itself by presenting high sensitivity, great selectivity, speed of analysis, which is very attractive options for the analysis of these compounds. For this reason, the aim of this project is to develop new methods for determination of compounds of high value added originating from vinasse of cane sugar. Thus, the project has the following objectives: a) development of new electrochemical sensors based on molecularly imprinted polymers anchored on graphene for determination of polyols in vinasse and b) development of new electrochemical sensors based on metallic nanoparticles anchored on graphene, coupled the chromatographic technique for determining carboxylic acids and amino acids vinasse.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

A modified glassy carbon electrode was developed to analysis of amino acids in sugarcane vinasse by ion chromatographic using pulsed electrochemical detection. The modification of glassy carbon electrode (GCE) with graphene oxide and nickel nanoparticles (NiNPs-RGO/GCE). Chromatographic separations were performed by using an anion-exchange column and isocratic elution. The separation of the amino acids was complete within 15 min. The value found in the sample was $1.5\times10^{-3} \pm 2.4\times10^{-5}$ mol L^{-1} (Alanine), $1.4\times10^{-2} \pm 4.0\times10^{-4}$ mol L^{-1} (Glycine) and $2.3\times10^{-2} \pm 4.5\times10^{-4}$ mol L^{-1} (Leucine) of sugarcane vinasse sample. The results demonstrate that the developed detector can be used to detect amino acids coupled with an anion-exchange column in quantitative analysis of amino acids, free of interferents and good accuracy in sample of sugarcane vinasse.

In another work we studied the electrochemical behavior of polyols in electrode modified with graphene containing copper oxide nanoparticles (CuNP/RGO/GCE) to be used as a sensor because these compounds do not exhibit electrochemical behavior in GCE unmodified. The voltammetric techniques used were cyclic voltammetry (CV) to characterize, the square wave electrode and voltammetry (SWV) and differential pulse (DPV) in order to search the most sensitive technique to operate the sensor. The electrode was characterized by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The CuNP/RGO/GCE showed lower charge transfer resistance (Rct), indicating that the electrode process is facilitated. From the SEM images it was observed that the nanoparticles are less than 100 nm and were distributed evenly on the graphene sheets. The polyols were analyzed separately and showed oxidation potential of 0.48 to 0.90 V, leading to the formation of formate ions and presenting irreversible behavior. The DPV was the best technique for quantification performance of these polyols, which is chosen for these studies on the construction of the sensor will be applied to the electrochemical determination of these compounds in vinasse sugarcane.

MAIN PUBLICATIONS

da Silva JL, Beluomini MA, Stradiotto NR. 2015. Chromatographic determination of amino acids in sugarcane vinasse using modified electrode with graphene oxide containing nickel nanoparticles. In: XX SIBEE. Uberlândia, Brasil, August 17-21, 2014.

Beluomini MA, da Silva JL, Stradiotto NR. 2014. Study to determine polyols in vinasse using electrode modified with copper nanoparticles in graphene by voltammetric techniques. In: XX SIBEE. Uberlândia, Brasil, August 17-21, 2014.

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