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Effect of Chitosan on the Volta Metric Response as an Electrochemical Sensor for the Detection of Iodide in Aqueous Solutions

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ABSTRACT

Iodide determination on carbon glass surfaces (CEMWG) and carbon glass modified with chitosan (GCEMCC) was carried out in chitosan concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5% (Fluka, high molecular weight) in acetic acid 2.0 M. Commercial potassium iodide (LAB-LINE 99.5% purity) was used for both electrodes at a concentration of 5.0 µg/mL. Cyclic Voltammetries (CV) and Differential Pulse Voltammetries (DPV) were carried out at pH 5.49. Obtained results show that with increasing concentrations of chitosan, the peak current (i_p) increases, reaching a maximum of 37.5 µA at a concentration of 1%. From here on, the peak current lowers as the chitosan concentration increases. When the chitosan concentration reaches 2.5%, the peak current is only 4.64 µA, which can be explained because of the chitosan high viscosity, slowing the electrons free movement towards the electrode surface, and thus, a smaller current response is obtained. When VC were carried out on the CEMWG and GCEMCC electrodes at 1% chitosan, using 0.2 M buffer acetic acid-sodium acetate as electrolyte solution (pH 5.49) and 2.0 µg/mL of KI, the oxidation signal of iodide was observed at +0.80V for the GCEMCC electrode, but was not observed for the CEMWG one, which indicates an increase in sensitivity of the modified electrode. DPV were also performed for both electrodes, at KI concentrations between 0.0 and 2.0 µg/mL, in order to get the minimum concentration of iodide that could be detected; the signal corresponding to the iodide oxidation appears at KI concentrations ≥ 0.75 µg/mL (E_P=+0.65 V), which improves 2 times the obtained signal in VC for CEMWG.

Keywords: *Chitosan, Glass Carbon, Electrochemistry, Voltammetry, Iodide*

1. INTRODUCTION

Iodine is usually obtained in many countries by iodization of salt or other foods like bread, seafood, cheese, eggs, and yoghurt. There are still regions in the world where people do not have the frequent opportunity to consume iodized food. The consequences of iodine deficiency in humans are mainly mental retardation, delayed growth and development, making this a bleak outlook scenario for millions of children in the world. Latin America is no exception to this reality, iodine deficiency in the population has had biological and social outcomes of enormous impact, which is usually seen in countries of low economic development and food deficiency. Iodine poor environments are typical of mountain areas. In 1996, the world regions with a stronger iodine deficiency were the Himalayas, the Andes, the Alps, mountains of China and generally the elevated areas and also in regions with heavy rainfall and frequent flooding, like in the deltas of large rivers [1]. According to the American Thyroid Association, in 2011, in a large part of the world, there was not enough available iodine in the humans' diet; nowadays iodine deficiency remains a major public health problem, approximately 40% of the world population continues to be at risk for iodine deficiency [2]. The main function of iodine in the body is to provide a substrate for the synthesis of thyroid hormones, Thyroxine (T_4) and Triiodothyronine (T_3), whose functions are to maintain optimal metabolism of all body tissues for normal performance. Thyroid hormones stimulate oxygen consumption and help to regulate the metabolism of fats and carbohydrates in the blood, but are especially important for normal growth and development. Iodide is the most common ionic form of iodine, rapidly absorbed from the gastrointestinal tract and is distributed in the extra cellular fluid [3,4]. That is why this work is based on the preparation of an electrochemical sensor for the detection of iodide, so it could be used in biological samples, since it is well known that electrochemical techniques are highly sensitive and may be used for the detection of this analyte in urine samples with indexes in the range of 0.10 to 0.20 µg/mL [5-9]. The modification technique of glassy carbon with a polymer in order to exploit its properties is well known; chitosan polymers provide properties of chelating agent and increments the selectivity in anion determination such as iodide. The presence of amino groups in the polymer chain of chitosan has converted this material in one of the most versatile and hence it has been studied for quite some time, including the possibility of a wide variety of modifications, such as ionic interactions, fixing reactions of enzymes, grafting reactions, production of cross linked films, etc., from which suitable materials are obtained for immediate and future applications in biotechnology, biomedicine and agriculture, among others [10].

2. MATERIALS AND METHODS

The electrochemical experiments were carried out using as the working electrodes glassy carbon electrodes unchanged (ECVSM) and chitosan modified glassy carbon electrodes (ECVMQQ). The diameter of the glassy carbon disk was 3.0 mm. We used a Ag/AgCl electrode saturated in 0.1 M KCl as reference and platinum as the counter electrode. All experiments were carried out at room temperature, atmospheric pressure and nitrogen saturation. The used cell was glass, with a single compartment with a three holes glass cover to insert the electrodes and two orifices for admission and release of gases. The potentiostat was an Autolab-USB PGSTAT12/30 analyzer connected to a Pentium 4 PC.

2.1 Preparation of the Working Electrode (GCUME)

The glassy carbon electrode was cleaned gently rubbing with 3 different sandpaper numbers, from broad to thin grain. It was then passed through a polishing wool of gamma-alumina 0.05 microns. Finally washed with doubly distilled water (18 MΩ).

2.2 Preparation of the Working Electrode(GCCCME)

The cleaning process was the same as for the unmodified electrode. Once cleaned, the electrode was dried with light radiation (OSRAN bulb, 200 W) for 10 minutes. It was left at room temperature for 10 more minutes and 10 µL of chitosan to the specified concentration was dropped. The electrode was then placed at 1 cm from the light bulb where it remained for 40 minutes. Finally the electrode was left at room temperature for 10 more minutes and ready to be used.

2.3 Activation of the Chemically Modified Chitosan Electrode (GCCCME)

The electrode activation was carried out by performing cyclic voltammetries in 0.01 M sulfuric acid of 10 consecutive scans in a potential window from 0.1 V to 1.2 V and at a scan rate of 100 mV/s, in the absence of N_2.

3. RESULTS AND DISCUSSION

3.1 Activation of the Electrode

To activate the electrode GCCCME, 1% chitosan was used and successive voltammetric scans were completed in a 0.01 M H_2SO_4 electrolyte solution in the absence of N_2, noting that for 10 successive scans, from the 8th scan onward the results were reproducible. As was expected, there is a notable difference between the 1st scan [voltammogram (a)] and the tenth one [voltammogram (d)] (see Figure 1).

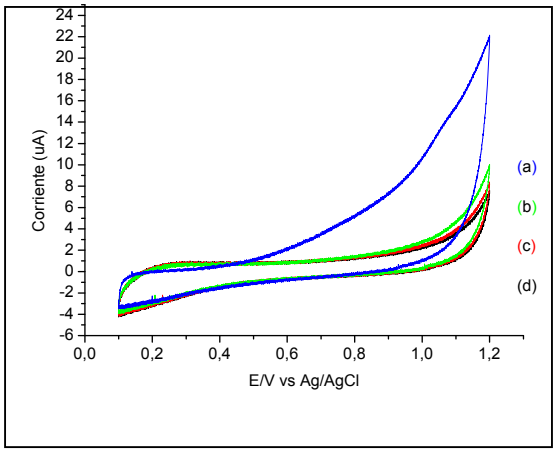

Fig 1: Successive cyclic voltammograms for the 1% GCCCME electrode in the absence of KI at a scan rate of 100 $mV.s^{-1}$: (a) 1st scan. (b) 5th scan. (c) 8th scan. (d) 10th scan. Supporting electrolyte of 0.01 M H_2SO_4 in the absence of N_2.

3.2 Location of the Iodide Oxidation Signal

Cyclic voltammograms were performed in the absence of potassium iodide at different scans on the 1% GCCCME electrode with H_2SO_4 0.01 M as supporting electrolyte and N_2 saturated atmosphere (see Figure 2), observing a slight increase in the currents as speed scans are increased. Then the same experiment was carried out but adding to the electrolytic solution 3 mL of potassium iodide 20 µg/mL, with a remaining concentration of iodide in the electrolytic cell equal to 2 µg/mL. In these voltammograms an oxidation peak is observed at near +0.80 V, with a slight shift to more positive potentials as the scan rate increases (see Figure 3).

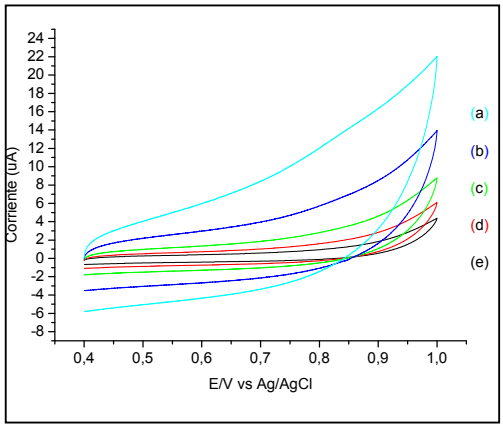

Fig 2: Cyclic voltammograms in the absence of potassium iodide on the 1% GCCCME electrode with H_2SO_4 0.01 M as supporting electrolyte and N_2 saturated atmosphere at scan rates of: (a) 100 $mV.s^{-1}$. (b) 50 $mV.s^{-1}$. (c) 20 $mV.s^{-1}$. (d) 10 $mV.s^{-1}$. (e) 5 $mV.s^{-1}$.

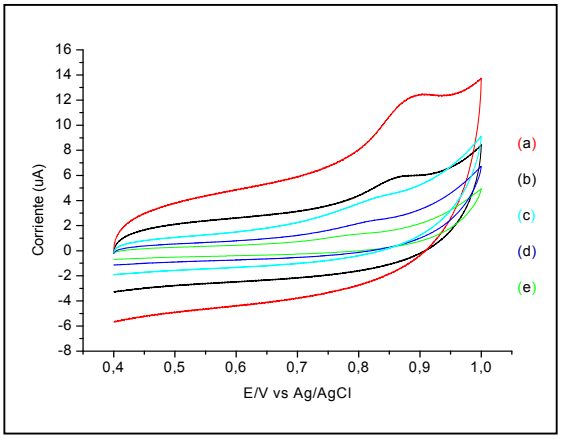

Fig 3: Cyclic voltammograms with 2 µg/mL potassium iodide on the 1% GCCCME electrode with H_2SO_4 0.01 M as supporting electrolyte and N_2 saturated atmosphere at scan rates: (a) 100 $mV.s^{-1}$. (b) 50 $mV.s^{-1}$. (c) 20 $mV.s^{-1}$. (d) 10 $mV.s^{1}$. (e) 5 $mV.s^{-1}$.

3.3 Cyclic voltammetries for GCCCME and GCUME 1% in acetic acid-sodium acetate 0.2 M (pH = 5.49) buffer and 2.0 µg/mL of KI.

Cyclic voltammetries for the GCCCME and GCUME 1% electrodes were carried out. The concentration of potassium iodide in the electrolyte solution (acetic acid-acetate sodium 0.2 M and pH=5.49 buffer) was 2.0 µg/mL for both electrodes (see Figure 4). The voltammogram (b) clearly shows the iodide oxidation signal at a potential of +0.80 V, which is not seen when using the GCUME as the working electrode [voltammogram (a)].

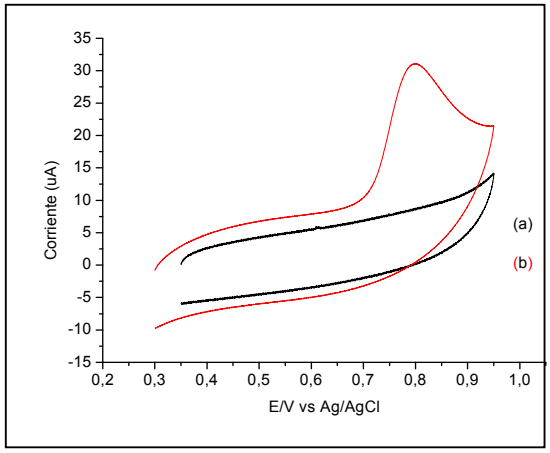

Fig 4: Cyclic voltammograms for electrodes: (a) GCUME and (b) GCCCME 1%. Acetic acid-sodium acetate 0.2 M (pH=5.49) as the supporting electrolyte and presence of potassium iodide 2.0 µg/mL. Saturated N_2 atmosphere

3.4 Differential pulse voltammetries for the GCCCME and GCUME 1% electrodes at potassium iodide concentrations under 2.0 µg/mL in acetic acid-sodium acetate 0.2 M buffer (pH = 5.49)

In order to improve the detection limit and response sensitivity, we opted for Differential Pulse Voltammetry (DPV) experiments with GCCCME and GCUME 1% electrodes at potassium iodide concentrations under 2.0 µg/mL (between 0.0 and 2.0 µg/mL). Figure 5 shows the obtained voltammograms for the GCUME at KI concentrations of 0.0; 0.025; 0.05; 0.10; 0.25; 0.50; 0.75; 1.0 and 2.0 µg/mL. Here we note that the iodide oxidation signal appears at KI concentrations ≥ 0.75 mg/mL (E_p=+0.65 V) getting less positive with increasing KI concentration. This improved response is about twice that obtained in CV for the GCUME (values not reported).

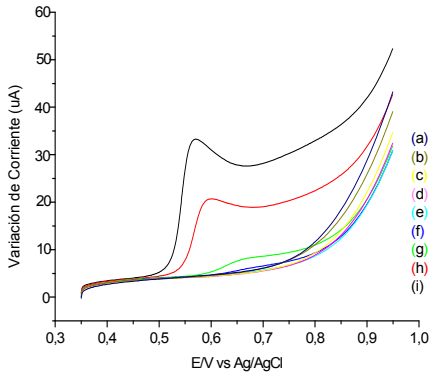

Fig 5: Differential pulse voltammograms for GCUME electrodes at different concentrations of potassium iodide: (a) 0.0 µg/mL. (b) 0.025 µg/mL. (c) 0.05 µg/mL. (d) 0.10 µg/mL. (e) 0.25 µg/mL. (f) 0.50 µg/mL. (g) 0.75 µg/mL. (h) 1.0 µg/mL. (i) 2.0 µg/mL. Acetic acid-sodium acetate 0.2 M as supporting electrolyte and saturated N_2 atmosphere.

To better visualize the voltammograms obtained in Figure 6, the results for the electrodes GCCCME and GCUME 1% at 1.0 µg/mL potassium iodide concentration are shown. This figure shows a clear difference between the two voltammograms, noting that for the GCCCME 1% the peak current is 15.82 µA while for the GCUME electrode is only 2.6 µA, this indicates a greater sensitivity of the GCCCME 1% electrode as compared to the GCUME electrode.

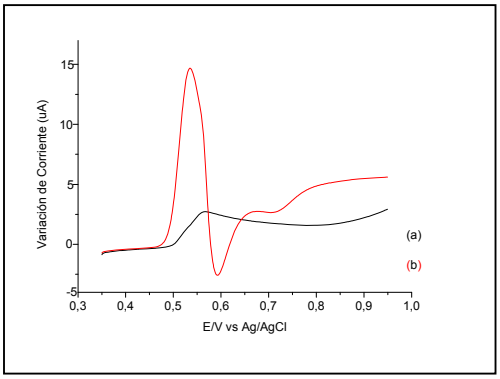

Fig 6: Differential pulse voltammograms for electrodes: (a) GCUME and (b) 1% GCCCME, and 1.0 µg/mL potassium iodide at pH 5,49. Potential window from 0.35 V to 0.95 V. Acetic acid-sodium acetate 0.2 M as supporting electrolyte and N_2 saturated atmosphere.

Figure 7 shows voltammograms obtained for the 1% GCCCME at KI concentrations equal to 0.0; 0.025; 0.05; 0.10; 0.25; 0.50; 0.75; 1.0 and 2.0 µg/mL. Here we observe that with increasing concentration of KI (equal or greater than 1.0 µg/mL), a signal appears close to +0.69 V. This is why it was decided to adjust the potential window for a better resolution; the new window was taken to be between 0.35 V and 0.95 V (Fig. 8). Before this adjustment the corresponding response to the iodide was no different from that of the unmodified electrode (figure 5), since both appear at a minimum iodide concentration of 0.75 µg/mL, except that for the modified electrode a better resolution is obtained with a higher current value and clearly shifted to more positive potentials. After selection of the potential window from 0.35 V to 0.95 V, DPV was again carried out for the 1% GCCCME electrode to different concentrations of KI (Figure 8). Results show the iodide oxidation signal for KI concentrations ≥ 0.10 µg/mL [voltammograms (d), (e), (f), (g) and (h)], improving the resolution of the obtained signals and strongly decreasing the detection limit.

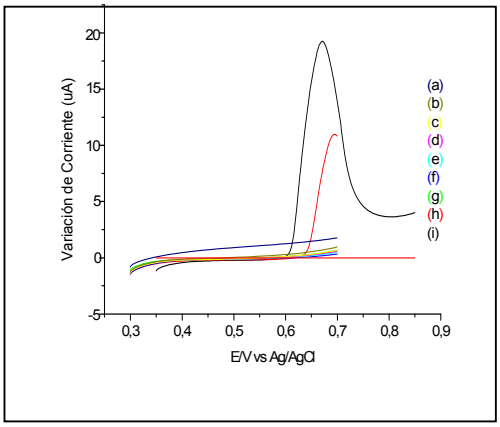

Fig 7: Differential pulse voltammograms for the 1% GCCCME electrode at potassium iodide concentrations of: (a) 0.0 µg/mL. (b) 0.025 µg/mL. (c) 0.05 µg/mL. (d) 0.10 µg/mL. (e) 0.25 µg/mL. (f) 0.50 µg/mL (g) 0.75 µg/mL. (h) 1.0 µg/mL. (i) 2.0 µg/mL, with a potential window from 0.30 to 0.70 V and from 0.30 to 0.85 V. Acetic acid-sodium acetate 0.2 M as support electrolyte and saturated atmosphere N_2.

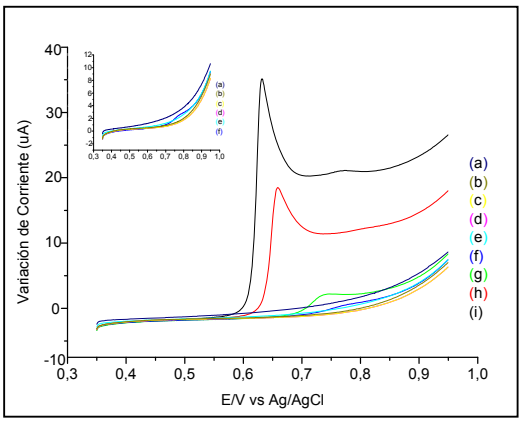

Fig 8: Differential pulse voltammograms for the 1% GCCCME electrode at potassium iodide concentrations: (a) 0.0 µg/mL. (b) 0.025 µg/mL. (c) 0.05 µg/mL. (d) 0.10 µg/mL. (e) 0.25 µg/mL. (f) 0.50 µg/mL (g) 0.75 µg/mL. (h) 1.0 µg/mL. (i) 2.0 µg/mL, with a potential window from 0.35 to 0.95 V. Acetic acid-sodium acetate 0.2 M as the support electrolyte and saturated atmosphere N_2.

The inserted box show voltammograms (a) through (f), with an enlarged scale where obtained peak current is better seen [(d), (e) and (f)], as well as its absence in others [(a), (b) and (c)].

3.5 Optimization of pH for 1% GCCCME in acetic acid-sodium acetate 0.2 M buffer (pH = 5.49) and KI at 2.0 µg/mL

Table 1 shows the peak currents obtained at different pH values for 1% GCCCME electrodes and a KI concentration of 2.0 µg/mL. The results showed that the larger peak current was reached at a pH of 5.49, with a value of 63.9 µA. It may be observed that there is a direct relationship between pH and the peak current, which may be explained since at high pH values, there are less H^+ ions, so that the NH_2 groups of chitosan are very little protonated and what the 1% GCCCME electrode really senses are the iodides in solution, whose concentration is 2.0 µg/mL. At lower pH (more H^+ ions) on the other hand, mainly iodides ions bound to chitosan are sensed, in which the NH_2 groups would be protonated.

Table 1: Peak currents obtained at different values of pH for 1% GCCCME electrodes and a KI concentration of 2.0 µg/mL.

pH	2.56	3.67	4.38	5.49
i_p(µA)	15.8	28.6	32.2	63.9

Furthermore, the effect of the iodide ions linked to the chitosan via the —NH_3^+ groups combined to the excess iodide in solution is likely what is obtained at the pH of 5.49. At pH values above 7.00 (alkaline values) there would be OH^- ions in solution, competing with the I^- ions for the —NH_3^+ groups, producing lower peak currents values corresponding to the iodide ions detection. This is consistent with what was stated by Pereira et al in 2006 and Hassan et al in 2010; these authors stated that the iodide oxidation occurs in several stages, which involves an adsorption-desorption process. They reported that the electrochemical oxidation of iodide includes adsorbed species and species in the solution and it follows as [11, 12]:

$$2I^- (sol) + I^- (ads) \rightarrow I_3^- (ads) + 2e^-$$
$$2I^- (sol) + I_3^- (ads) \rightarrow I_5^- (ads) + 2e^-$$

and/or

$$2I^- (sol) + I^- (ads) \rightarrow I_2\text{----}I^- (ads) + 2e^-$$

followed by:

$$I_5^- (ads) \rightarrow I_2 (sol) + I_3^- (ads)$$

and/or

$$I_2\text{----}I^- (ads) \rightarrow I_2 (sol) + I^- (ads)$$

3.6 Determination of chitosan percentage for the GCCCME electrodes preparation using as the electrolytic buffer solution acetic acid-sodium acetate 0.2 M (pH= 5.49) and 0.10 µg/mL of KI

Figure 9 shows the peak currents obtained for the different chitosan concentrations studied for GCCCME electrodes at a pH of 5.49 and a KI concentration of 0.10 µg/mL. These results showed that the higher peak current is reached at 1% chitosan, with an approximate value of 37.50 µA. When the chitosan concentration is raised to 2.5%, the peak current lowers to 4.64 µA, which is justified because of the high chitosan concentration (high viscosity), preventing the free electrons movement to the surface electrode giving a smaller response.

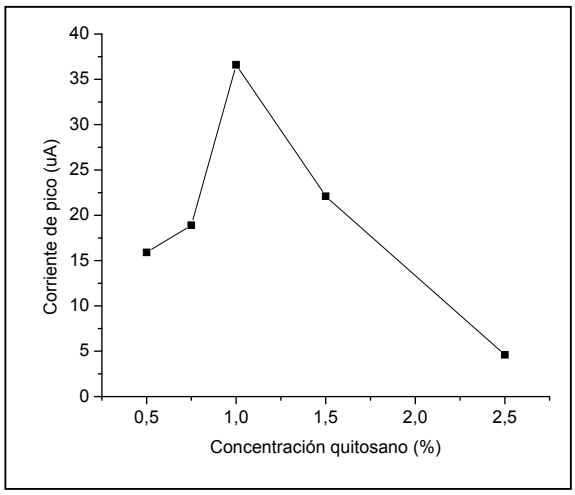

Fig 9: Peak currents as a function of chitosan concentration at pH 5.49 for GCCCME electrodes and a KI concentration of 0.10 µg/mL.

4. CONCLUSION

a. The surface modification carried out to the glassy carbon electrode with chitosan, significantly improved the properties of the glassy carbon as substrate. The transformed glassy carbon surfaces with chitosan showed good affinity and sensitivity for iodide immobilization and subsequent detection and quantification (adsorbed and in solution).

b. It is important to point out that fixing the chitosan in the glassy carbon electrode by the dry process with light radiation, was decisive in the results, since experiments carried out without this step did not lead to a direct relationship between i_p and iodide concentration, observing noisy voltammetric responses, and hence we must assume that chitosan emission from the electrode surface is produced.

c. The low detection limit and good sensitivity was a major goal in this work, since the main objective in the preparation of this sensor (GCCCME electrode) is its future application in iodide detection in urine samples, whose reference values range from 0.10 to 0.20 µg/mL. With this electrode it was possible to measure iodide concentrations as low as 0.10 µg/mL, which is a 10 times greater sensitivity than the unmodified electrode (GCUME).

d. The voltammetric techniques remain invaluable tools for the detection of low analyte concentrations. Cyclic voltammetry (CV) was mainly used for the diagnosis and characterization of the supports, whereas the differential pulse voltammetry (DPV) was used to improve the detection limit and sensitivity of the CV.

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