

Ascorbic acid determination using a carbon paste electrode modified with iron(III) ions adsorbed on humic acid

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Abstract: An amperometric sensor was constructed, by using humic acids to immobilize Fe^{3+} ions on a carbon paste electrode (CPE-HA-Fe), and used for ascorbic acid (H_2A) determination. The cyclic voltammogram of the electrode showed electrochemical response due to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at $E_{1/2}=+0.78$ V vs SCE, using 0.5 mol L^{-1} KCl and 0.2 mol L^{-1} acetate/ 0.020 mol L^{-1} phosphate buffer, at $\text{pH} = 5.4$, as supporting electrolyte. When H_2A is added to the electrolyte solution it is observed an oxidation process. The oxidation current, obtained by chronoamperometry at $+0.87$ V vs SCE, is proportional to the concentration, represented by the equation $I(\mu\text{A}) = 7.6286 [\text{H}_2\text{A}] (\text{mmol L}^{-1}) + 1.9583$, $r = 0.9996$, for concentrations between 0.0 and 1.4 mmol L^{-1} . The electrode showed high stability and was used for H_2A determination in a natural orange juice.

Keywords: carbon paste electrode; humic acids; iron(III) ions; ascorbic acid.

Introduction

Many efforts have been made to the development of new chemically modified electrodes, which can be used as simple and rapid analytical test for determining concentrations of important substances. Different materials, as polymers [1], oxides [2], zeolites [3], inorganic or organic films [4,5], have been used to immobilize different electroactive species on electrode surfaces to use as amperometric sensors.

Humic substances are organic compounds largely distributed in natural soil and water, representing about 80% of the organic matter in these systems [6-8]. They result of vegetal and animal residues in advanced stages of decomposition and strongly influence the soil properties, as capacity of ions adsorption, pH, color, heat retention, permeability, and others. Humic acids are the fraction of the humic substances that are extracted by dissolution in strongly alkaline medium and precipitated in acid medium. They are formed by molecules of high molecular weigh, in a complex structure, not completely understood, but basically composed by C, H, N

and O, with a more or less aromatic character. Humic acids also show a large number of acid sites, carboxylic and phenolic hydroxylic groups, which are responsible for the capacity of adsorption of cations.

Due to this property, humic acids have been used as modifiers in the construction of carbon paste electrodes (CPE-HA) [9-15]. These electrodes were used to voltammetric detection of metal ions. The method is based on metal ion adsorption on the electrode surface at the humic acid sites, application of a negative potential to reduction and scan of potential to positive values. The current obtained due to oxidation is proportional to the metal ion concentration initially present at the solution. Electroanalytical techniques such as cyclic, square wave or anodic stripping voltammetry have been used to characterization and use of these electrodes.

But the use of humic acids as modifiers to immobilize metal cations at carbon paste electrodes to act as electrocatalysts for oxidation or reduction process of other species present in solution, and the use of the electrode as amperometric sensors for this specie, in our knowledge, was not

reported in the literature. This is the objective of this work. It was described the construction of a carbon paste electrode modified with humic acids to immobilize iron(III) ions and the use as amperometric sensor to determine ascorbic acid (H_2A).

Experimental details

Reagents and apparatus

L-ascorbic acid (Reagen), $Fe(NO_3)_3 \cdot 9H_2O$ (Vetec), and other chemicals were of analytical reagent grade. All electrochemical measurements were performed on a potentiostat model MQPG-01 (Microquímica). A three electrode system was used, with a platinum sheet and saturated calomel electrode (SCE) as auxiliary and reference electrodes, and a carbon paste electrode with Fe^{3+} ions immobilized by use of humic acid (CPE-HA-Fe) as a working electrode. As supporting electrolyte, 0.5 mol L^{-1} potassium chloride (Reagen) and 0.2 mol L^{-1} sodium acetate (Merck)/0.02 mol L^{-1} sodium phosphate (Merck) buffer were used, with the pH controlled by addition of 6 mol L^{-1} acetic acid (Merck) or NaOH (Synth). All solutions were prepared with distilled and deionized water, in a Quimis system, and the measurements were made in N_2 (White Martins) atmosphere at 25°C.

Preparation of the carbon paste electrode

Humic acid was extracted from a soil sample collected in a drained bog in Coronel Bicaco city, Rio Grande do Sul state, Brazil (27°42'56" S, 53°42'05" W). The soil sample was air dried and triturated. The organic matter amount was determined by heated sulphochromic solution oxidation and spectrophotometric Cr^{3+} determination [16]. Humic acid was extracted in accord with the standard method recommended by the International Humic Substances Society (IHSS) [8], using 1 mol L^{-1} NaOH for dissolution, HCl until pH=1 for precipitation, and purification with HF/HCl 1%. Ash content in the extracted humic acid was determined by calcinations at 700°C for 5h.

Iron(III) ions were adsorbed on the humic acid by addition of the solid sample (100 mg) to 50 mL of 2×10^{-2} mol L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ solution, at pH=6.5 (adjusted with 6 mol L^{-1} HNO_3 or NaOH solutions). The mixture was stirred for 10 h, and the solid was filtered, washed and dried on vacuum at 45°C for 15 h. This material will be represented by AH-Fe. The amount of iron ions adsorbed was determined by calcinations of the

solid at 750°C for 7 h. The residue was dissolved in concentrated HNO_3 , and the volume was completed to 25 mL with 1 mol L^{-1} HNO_3 . The iron content was determined by atomic absorption spectrometry using a Perkin Elmer spectrometer.

Finally, the carbon paste electrode, CPE-HA-Fe, was constructed by mixing 10 mg of graphite powder (Merck), 5 mg of AH-Fe and one drop of mineral oil (Nujol).

Electrocatalytic determination of L-ascorbic acid

For the electrocatalytic studies, L-ascorbic acid was added to the supporting electrolyte solution at the desired concentrations. To analyze H_2A in a real sample, a natural juice obtained directly from orange was used. The H_2A concentration was determined by chronoamperometry using the CPE-HA-Fe electrode and the results were compared with the results obtained by the iodometric method [17]. The measurements were repeated forty times.

Results and Discussion

Soil and humic acid characterization

The soil sample organic matter content was 7.1%, and it was obtained 0.94% of humic acid in the extraction process. Practically no ash was found in the extracted humic acids, indicating that the extraction was efficient. The content of iron ions adsorbed by the humic acid was 0.57 mmol g^{-1} .

Electrochemical characterization of the CPE-HA-Fe

In Fig. 1a is represented the cyclic voltammogram obtained for the CPE-HA-Fe electrode. It was observed a reversible process at $E_{1/2} = +0.78$ V vs SCE, where $E_{1/2}$ is the half-wave potential, $E_{1/2} = (E_{pa} + E_{pc})/2$, and E_{pa} and E_{pc} are anodic and the cathodic peak potentials. The peak separation between the two peak potentials was 0.27V, at a scan rate of 10 $mV s^{-1}$. This response may be attributed to the Fe^{2+}/Fe^{3+} process. No response is observed for the electrode constructed with humic acid with no Fe^{3+} ions (CPE-HA) (Fig. 1c).

The half-wave potential at this positive region indicates that the Fe^{2+} is the species present at the humic acid sites, indicating that there is reduction of the Fe^{3+} ions when adsorbed. In studies reported on literature it was also observed the capacity of humic acids to reduce Fe^{3+} ions [18].

Fig. 2 shows the dependence of $E_{1/2}$ with pH. Decreasing pH, $E_{1/2}$ shifts to more positive values. The same dependence was also observed

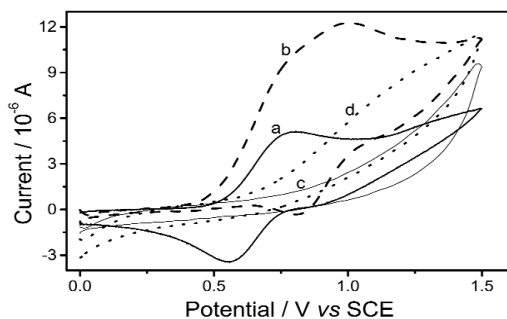


Figure 1. Cyclic voltammogram of the CPE-HA-Fe electrode in absence (a) and presence of 2 mmol L⁻¹ ascorbic acid (b), and of the CPE-HA electrode in absence (c) and presence of 2 mmol L⁻¹ ascorbic acid (d); pH = 5.4; scan rate of 10 mV s⁻¹.

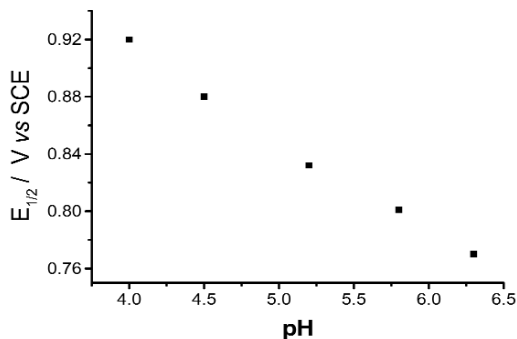


Figure 2. Half-wave potentials ($E_{1/2}$) obtained, by cyclic voltammetry at scan rate of 25 mV s⁻¹, for the CPE-HA-Fe electrode at different pH values.

for Fe³⁺/Fe²⁺ couple in solution. In cyclic voltammetric experiments using Fe(NO₃)₃ 1 mmol L⁻¹ at the same solution conditions, it was observed $E_{1/2} = -0.25$ and $+0.35$ V vs SCE at pH values of 6.5 and 2.0, respectively. It indicates that this dependence of $E_{1/2}$ with pH is not due to specific interaction of the ion with the humic acid, and is in accord with the literature, which attributes the easier oxidation of Fe²⁺ at higher pH values to the hydroxo complex formed by the Fe³⁺ specie [19]. Comparing $E_{1/2}$ observed for Fe³⁺/Fe²⁺ couple in solution and adsorbed in the humic acid it is observed more positive values for the humic acid immobilized ions, indicating that complexation to the carboxylate groups stabilizes the Fe²⁺ specie.

Electrocatalytic determination of L-ascorbic acid

When H₂A is added to the electrolyte solution, it is observed an increase in the anodic and a little decrease in the cathodic peak current

in the cyclic voltammogram (Fig. 1). It is due to electron transfer from dissolved H₂A to oxidized immobilized Fe³⁺ ions, indicating electrocatalysis of the H₂A oxidation. Using CPE-HA electrode significant H₂A oxidation is observed only at higher potentials (Fig. 1d).

In Fig. 3 is shown the intensity of the current observed for H₂A oxidation as a function of the applied potential, obtained by chronoamperometry. It is observed that the electrocatalytic process begins at +0.2 V, and the current increases until +0.87 V vs SCE. At more positive potentials the current remains constant.

The current (I), obtained by chronoamperometry, for H₂A oxidation at a fixed potential (+0.87 V vs SCE), is shown in Fig. 4. It was obtained a linear relationship with the concentration of dissolved H₂A in aqueous solution, described by the equation $I(\mu\text{A}) = 7.6286 [\text{H}_2\text{A}]$ (mmol L⁻¹) + 1.9583, with a linear correlation coefficient $r = 0.9996$, for H₂A concentrations between 0.0 and 1.4 mmol L⁻¹. In accord with this result, this electrode is proposed to be used as a sensor for ascorbic acid in aqueous solution.

Recovery test was performed using a natural orange juice, and the result was very good. The H₂A concentration obtained, using chronoamperometry, by the CPE-HA-Fe electrode was 42.1 ± 1.8 mg/100 mL, and by the use of iodometric method [17] was 42.9 ± 2.2 mg/100mL.

The CPE-HA-Fe electrode showed high stability. It was used continuously for 52 h and no decrease in the peak currents was observed. After 52 h there is a gradual decrease of the current, and after 180 h the response is not observed anymore, and is necessary renovation of the surface.

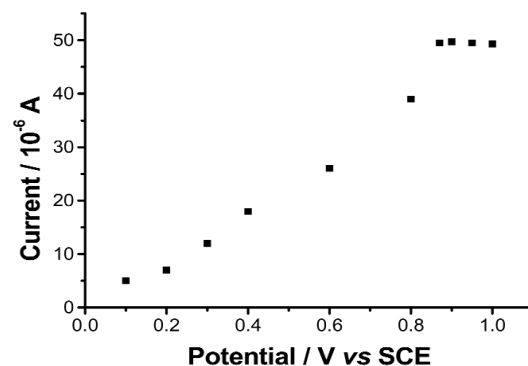


Figure 3. Current due to ascorbic acid oxidation at CPE-HA-Fe electrode, as a function of the applied potential, obtained by chronoamperometry, in 2 mmol L⁻¹ ascorbic acid at pH = 5.4.

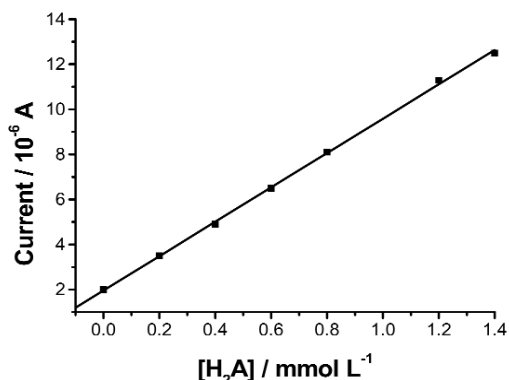


Figure 4. Current due to ascorbic acid oxidation at CPE-HA-Fe electrode, as a function of ascorbic acid concentration, obtained by chronoamperometry at +0.87 V vs SCE; pH = 5.4.

Conclusions

The humic acid was very efficient to

L. S. Silva, T. N. Oliveira, M. A. Ballin, C. R. M. Peixoto. Determinação de ácido ascórbico usando eletrodo de pasta de carbono modificado com ions ferro(III) adsorvidos em ácido húmico.

Resumo: Um sensor amperométrico foi construído, usando-se ácidos húmicos para imobilização de íons Fe³⁺ em eletrodo de pasta de carbono (CPE-HA-Fe), e usado para determinação de ácido ascórbico (H₂A). O voltamograma cíclico do eletrodo apresentou resposta eletroquímica devido ao par Fe³⁺/Fe²⁺ a E_{1/2}=+0.78 V vs ECS, em eletrólito suporte KCl 0,5 mol L⁻¹ e tampão acetato 0,2 mol L⁻¹ /fosfato 0,020 mol L⁻¹, a pH = 5,4. Quando H₂A é adicionado à solução eletrolítica é observado processo de oxidação. A corrente obtida cronoamperometricamente a +0,87 V vs ECS, devido ao processo de oxidação, é proporcional à concentração, de acordo com a equação $I(A) = 7,6286 [H_2A] (mmol L^{-1}) + 1,9583$, $r = 0,9996$, para concentrações entre 0,0 and 1,4 mmol L⁻¹. O eletrodo apresentou alta estabilidade e foi usado para determinação de H₂A em suco de laranja natural.

Palavras-chave: eletrodo de pasta de carbono; ácidos húmicos; íons ferro(III); ácido ascórbico.

References

- [1] J. O. Pontólio, N. Ferranti, M. L. A. M. Campos, and J. R. Romero, *J. Electroanal. Chem.* 584 (2005) 124.
- [2] W. S. Cardoso, and Y. Gushikem, *J. Electroanal. Chem.* 583 (2005) 300.
- [3] M. M. Ardakani, Z. Akrami, H. Kazemian, and H. R. Zare, *J. Electroanal. Chem.* 586(2006)31.
- [4] M. H. Pournaghi-Azar, and H. Nahalparvari, *J. Electroanal. Chem.*583 (2005) 307.
- [5] X. Lin, C. Jiang, *Anal. Sci.* 22 (2006) 697.
- [6] F. J. Stevenson, *Húmus Chemistry: Genesis, composition, reactions*, John Wiley & Sons, INC., New York, 2^a ed., 1994.
- [7] J. C. Rocha, A. H. Rosa, *Substâncias Húmicas Aquáticas, Interação com Espécies Metálicas*, Ed. Unesp, São Paulo-SP, 2003.
- [8] R. S. Swift, in: *Methods of Soil Analysis Part 3: Chemical Methods (SSSA Book Series No.5.)*, Sparks, D.L. ed., SSSA and ASA, Madison, WI, 1996.
- [9] M. O. O. Rezende, and F. N. Crespilho, *Quim. Nova* 27 (2004) 964.
- [10] W. T. L. Silva, C. Thobie-Gautier, M. O. O. Resende, and N. El Murr, *Electroanalysis* 14 (2002) 71.
- [11] C. Wang, B. Zhu, and H. Li, *Electroanalysis* 11 (1999) 183.
- [12] C. Wang, H. Zhang, Y. Sun, and H. Li, *Anal. Chim. Acta* 361 (1998) 133.
- [13] Q. Y. Sun, C. M. Wang, L. X. Li, and H. L. Li, *Fresenius J. Anal. Chem.* 363 (1999) 114.
- [14] Z. Navratilova, and P. Kula, *Anal. Chim. Acta* 273 (1993) 305.
- [15] C.D. García, and P.I. Ortiz, *Talanta* 61 (2003) 547.
- [16] M. J. Tedesco, C. Geanello, C. A. Bissani, H. E. Bohnen, and S. A. J. Volkweiss, *Análises de Solo, Plantas e Outros Materiais*, Departamento de Solos, Faculdade de Agronomia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, 1995.
- [17] IMESP, *Normas Técnicas do Instituto Adolfo Lutz*, São Paulo, SP, Brasil, 1985.
- [18] G. Sposito, *The Chemistry of Soils*, Oxford University Press, New York, 1989.
- [19] F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, sixth ed., John Wiley & Sons, Inc., New York, 1999.

immobilize Fe³⁺ ions on a carbon paste electrode. The metal ion maintained the electrochemical response and the capacity of electron transfer, demonstrated by the electrocatalysis of the ascorbic acid oxidation. The high stability of the electrode and linearity of the current with the concentration of the ascorbic acid permitted the use of the electrode as an amperometric sensor.

Humic acid is an abundant material on the nature and may be obtained at low cost. This study demonstrates that humic acid is a suitable material for immobilizing metal ions on electrodes. Other electrodes may be constructed using other metal ions to be used as sensors for other species.

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