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Development of chemically modified carbon paste electrodes with transition metal complexes anchored on silica gel

Bárbara B. Cazula, Angélica M. Lazarin*

Departamento de Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, PR, Brazil

HIGHLIGHTS

- The chemically modified silica gel adsorbed whit nickel (II) and cobalt(II) metallic ions complex was prepared.
- These newly synthesized compounds were incorporated into a carbon paste electrode.
- The electrodes did not show significant changes in response after six months of use.
- The modified electrodes are very stable and reproducible.
- The electrodes sensors were successfully applied for B_6 Vitamin and dopamine determination.

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ABSTRACT

The chemically modified silica gel with 3-(2-aminoethyl)aminopropyl]trimethoxysilane groups and *p*-aminobenzoic acid was used to immobilize the nickel (II) and cobalt(II) metallic ions complex initially. These materials were incorporated into a carbon paste electrode and its electrochemical properties were investigated. However, for dopamine and B_6 vitamin solution, an enhancement of the anodic peak current was detected due to electrocatalytic oxidation. The electrodes presented the same response for at least 150 successive measurements, with a good repeatability. The modified electrodes are very stable and reproducible. The sensors were applied for dopamine and B_6 vitamin determination in pharmaceutical preparation with success.

1. Introduction

Of the various works found in literature elated to the preparation of chemically modified silica, a special attention to those that involve modifying materials containing transition metal ions forming supported complex, on its surface and they are used in the construction of chemically modified electrodes (CME), together with carbon paste electrodes (CPE) on the electrochemical behavior of the study of these complexes anchored in electroanalysis and electrocatalysis [1–6]. The advantages of the use of organically modified silica, containing on its surface the sequestering agent for transition metals, such as Co(II) and Ni(II), are related to their high thermal stability, the accessibility of reactive centers and its insolubility in organic means [7–9].

Electrochemical methods are powerful and versatile analytical techniques that offer high sensitivity, accuracy, and precision as well as large linear dynamic range, with relatively low-cost instrumentation. After developing more sensitive pulse methods, the electroanalytical studies are more regularly used on industrial, environmental applications and on the drug analysis in their dosage forms and especially in biological samples. However, electroanalytical techniques can easily solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity, and selectivity employing this approach. Some of the most useful electroanalytical techniques are based on the concept of continuously changing the applied potentials to the electrode-solution interface and the resulting measured current. Most of the chemical compounds were found to be as electrochemically active. During the past years, there has been extraordinary acceleration of progress in the discovery, synthesis, sensitive

* Corresponding author.
E-mail address: amlazarin2@uem.br (A.M. Lazarin).

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electrochemical analysis [10–15].

Applications and the development of chemically modified electrodes in electrochemistry and electroanalytical have been extensively reviewed [1–3,16,17], as the chemically modified electrodes have characteristics such as selectivity, high sensitivity and simplicity of monitoring the analyte of interest, without prior treatment of the sample [18].

The present investigation deals with the electrochemical behavior of nickel (II) and cobalt(II) metallic ions complex immobilized on silica gel surface chemically modified with 3-(2-aminoethyl)aminopropyl]trimethoxysilane groups and *p*-aminobenzoic acid. This newly synthesized compound was first used to prepare a carbon paste electrode and the resulting material was tested for dopamine and B_6 vitamin oxidation. An electrochemical procedure, using an innovative, stable innovator inorganic support, is now proposed. This new complex synthesized incorporated in carbon paste electrode has many advantages when compared with other complexes synthesized [19,20], such as easily in preparation, good chemical stability, reproducibility, fast response time. The new material can be used as a sensor for dopamine and B_6 vitamin.

The pyridoxine (B_6 vitamin) performs an important role in the synthesis of neurotransmitters, such as dopamine, and also participate in amino acids degradation reactions. The dopamine (DA) is an important neurotransmitter in the central nervous system of mammals whose concentration in the extracellular fluid is lower than that of ascorbic acid (AA). The voltammetric response with glassy carbon electrode for dopamine suffers, so the interference of ascorbic acid, which coexists in vivo, in the extracellular fluid of the basic central nervous system as the anion of high concentration and has oxidation potential close to that of dopamine (lowest concentration) [21].

2. Experimental

2.1. Materials

All chemicals used were of reagent grade and deionized water was employed throughout the experiments. Silica Gel (Merck), [3-(2-aminoethyl)aminopropyl]trimethoxysilane (Synth), *p*-aminobenzoic acid (Aldrich), ethanol (Synth), nickel chloride (Synth) and cobalt chloride (Synth) were used for all preparations. Graphite (Fluka), the pyridoxine (Merck) and dopamine (Merck) were used.

2.2. AETS modified agent coated on the silica gel surface

Silica gel functionalized with [3-(2-aminoethyl)aminopropyl] trimethoxysilane group was obtained according to the reaction:

$$\equiv Si(OH)_3 + (CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2 \quad \equiv SiO_3Si(CH_2)_3NH(CH_2)_2NH_2 + 3CH_3OH \tag{1}$$

SF AETS SF-AETS

Silica gel was degassed at 423 K under vacuum (10^{-3} atm) for 8 h. About 50 g this material was mixed with 30.0 cm^3 of [3-(2-aminoethyl)aminopropyl] trimethoxysilane dissolved in 400 cm^3 of dry toluene. The mixture was stirred for 12 h under a dry nitrogen atmosphere at the temperature of the solvent reflux. The chemically modified silica was separated by filtration, washed with ethanol in a Soxhlet extractor for 24 h and finally dried at 353 K under vacuum (10^{-3} atm). The solid was named SF-AETS.

2.3. Modification of the SF-AETS silica with PABA

In 10 g of SF-AETS silica suspended in 50.0 cm^3 of dry ethanol, PABA reagent was added (1.7×10^{-3} mol). The mixture was refluxed under mechanical stirring for one hour, then filtered and washed with ethanol and anhydrous ethyl ether. Excess solvent was removed by placing the silica in oven at 323 K for 6 h. The silica obtained was SF-AETS/PABA.

2.4. Characterization

The amount of nitrogen in the sample of SF-AETS was quantified taking advantage of its basic character [22]. In a typical example, 0.200 mg of the SF-AETS silica were added to 25.0 cm^3 of standard HCl (0.104 mol dm^{-3}) solution in a thermostatized cell (298 K), reacting for one hour. The conductivity of the system was measured before and after the reaction. The excess of acid was determined by means of conductivity variation and used to calculate the amount of nitrogen sites.

The conductivity measurements were performed in a Conductivity CD-21 Digimed with immersion cell with platinized platinum electrode, using a magnetic shaker Tecnal TE 085 and bath thermostat Microquímica, MGBTZ 99-20 model with resolution ±0.1.

Infrared spectra of the samples were acquired from the pressed material in KBr disc with 1% (by weight) on a Perkin-Elmer FTIR spectrophotometer, model 1600, by using pressed KBr pellets in the 4000-400 cm^{-1} range with 4 cm^{-1} of resolution.

2.5. Adsorption isotherms

The adsorption isotherms for $NiCl_2$ and $CoCl_2$ in ethanol solutions were performed by using the batchwise method. For each isotherm, a series of samples containing 100 mg of SF-AETS/PABA was shaken for 2 h, as previously established, in an orbital bath with variable concentrations of each metal halide at a constant temperature of 298 ± 1 K. The concentration of the metal ion in solution in equilibrium with the solid phase was determined by direct titration with EDTA (0.010 mol dm^{-3}) using murexide and eriochrome black T as indicator. The amount of cations adsorbed, n_f, was determined by applying the equation: $n_f = (n_a - n_s)/m$, where m is the mass of the adsorbent and n_a and n_s are the initial and the equilibrium amounts of the metal in the solution phase in number of moles, respectively, which is a measure of the degree of coverage for each of the experimental conditions used, i.e.

$$n_f = \frac{n_a - n_s}{m} = \sum_m \frac{[(SF - AETS/PABA)_m MCl_2]}{m} \tag{2}$$

where the summation extends over all species on the surface. The maximum number of moles of the adsorbed complex $n_f^{máx}$ is equal

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