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Article

The Preparation and Characterization of the Hexacyanides Immobilized in Chitosan

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Mostramos neste trabalho alguns detalhes sobre a imobilização de complexos ferrocianeto e ferricianeto sobre a superfície do biopolímero quitosana. Os complexos imobilizados foram caracterizados por eletroquimica, espectrocopia de infravermelho e Mössbauer. Foi observado mudanças nos espectros de infravermelho e Mössbauer, e no voltamogramas cíclicos do material preparado com ferricianeto após exposição a luz do sol. Estas alterações indicam que o ferricianeto sofreu um processo de redução fotoinduzida na superfícies do biopolímero.

We report some details of the ferrocyanide and ferricyanide complexes immobilized in chitosan. These immobilized complexes are characterized by electrochemistry, and infrared and Mössbauer spectroscopy. Alterations are observed in the infrared and Mössbauer spectra and in the cyclic voltammograms of the material prepared with ferricyanide when this material is irradiated with sunlight. These alterations indicate that the ferricyanide ion undergoes a photoinductive reduction on the biopolymeric surface.

Keywords: *chitosan, cyclic voltammograms, photoinductive reduction*

Introduction

In recent years increased attention has been given to sunlight-induced photochemical effects. The photoreactivity of both organic and inorganic iron complexes has been recognized for a long time, and many reports on the effects of light on the chemistry of iron have been published over the last 100 years[1]. In this study the preparation and characterization of ferrocyanide and ferricyanide complexes immobilized in chitosan is described. Chitosan is a polysaccharide usually prepared by the N-desacetylation of chitin, through a basic hydrolysis reaction, and largely consists of glucosamine units and a smaller percentage of N-acetyl-glucosamine residues (Fig. 1)[2]. Chitosan has a similar structure to that of cellulose, but shows many properties that differ from the latter, for example, chitosan is considered more chemically versatile than cellulose, due to the presence of an amino group. This group gives chitosan solubility in organic acids (acetic acid, formic acid) and diluted inorganic acids (chloridric acid). This polymer has been the object of continued study for several decades. In particular, its metal-binding property has led to the use of chitosan as a low-cost material in, waste water treatment plants and streams contaminated by the accumulation of toxic metals released by industrial activities[3-5].

In a recent report chitosan was used in the immobilization and characterization of nitrite, permanganate, iodide and ferricyanide by stripping voltammetry with a

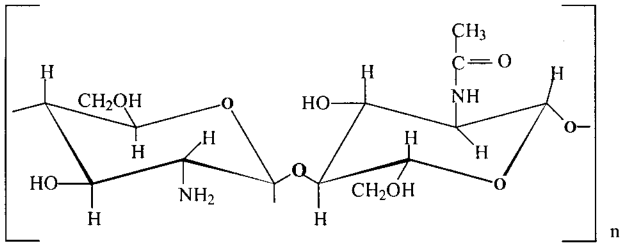

Figure 1. The chitosan structure[4]. The polysaccharide was prepared by the N-desacetylation of chitin.

modified carbon paste electrode (MCPE). The immobilization in the MCPE occurs through the electrostatic interaction between the NH_3^+ groups in the protonated chitosan (pH below 3.5) and the respective anions[6].

The chemically modified electrode (CME) for electroanalysis has increasingly been the subject of research. The electrodes are made by incorporating specific chemicals and grouping them on the electrode surface. The use of redox polymers as electrode modifiers to induce electrocatalysis has drawn considerable attention. Such polymers can provide a support for the site that mediates the exchange of electrons between the electrode and the solution[7].

The purpose of the present study is to prepare and characterize the ferricyanide and ferrocianyde adsorbed on the chitosan surface. This material was used in the preparation of the CME in an electrocatalysis experiment.

In the course of the characterization of the polymer redox, it was observed that the ion ferricyanide which was adsorbed on a chitosan surface underwent a photoinductive reduction process.

Experimental

Analytical grade potassium ferricyanide and ferrocyanide from Merck were used. Chitosan (20% N-acetylated) was prepared by the basic hydrolysis of chitin, following the method described in the literature[8,9]. The immobilization of the ferricyanide complex on a chitosan surface was done as follows: 0.6 g chitosan was immersed in a 0.1 M ferricyanide solution (50 mL) and the pH of this solution was adjusted to 3 using HCl. This solution was stirred for two hours and protected from light. The solid was subsequently filtered and exhaustively washed with distilled water to remove the excess ferricyanide, and was then dried under vacuum at room temperature. The immobilization of ferrocyanide was done in a similar way. The cyclic voltammograms were obtained using a cyclic voltammeter model CV-27 (Bioanalytic System, Inc.) connected to an X-Y Omnigraphic 100 register (Houston Instruments). A three-electrode system was used, with a carbon paste electrode as the working electrode, a (Ag/AgCl - KCl sat.) reference electrode and a platinum wire as the auxiliary electrode. The carbon paste modified electrode (CPME) was prepared by mixing 0.4 g of electrolytic carbon powder (Rekipro) with 0.2 g of mineral oil (Nujol) and 0.06 g of polymer. The paste was packed into glass tube, which gave a geometric surface area of approximately 0.07 cm^2. The infrared spectra were obtained in KBr disk on a IR-FT Bomen MB-100 spectrophotometer.

The Mössbauer spectra were obtained at room temperature, using 24 mCi ^{57}Co source in a matrix of Rh, and detected by a Kr-CO_2 proportional counter (Reuter Stokes) coupled to multichannel analyzer (EG&G ORTECH). The isomer shifts were calibrated with α-iron foils and referenced against sodium nitroprusside (line wide at one-half the maximum of 0.25 mm s^{-1}.

The Mössbauer spectra were adjusted by Lorentzian curves utilizing the "Normos" version PC[10], and decomposed using the Grapher program[11]. The measurements for the Mössbauer spectroscopy were obtained from solid samples of the ferricyanide ion complex immobilized on a chitosan surface irradiated with sunlight, and compared with free ferrocyanide and ferricyanide.

Results and Discussion

The presence of ferricyanide adsorbed on a chitosan surface can be observed by the greenish yellow coloration characteristic of this anion. This color gradually changes to a bluish shade when submitted to sunlight radiation. The same bluish shade is observed in the polymer sample prepared with ferrocyanide. The quantity of ferricyanide adsorbed on the polymer surface determined by the fluorescence of the X-ray was 2.74 x 10^{-3} mol g^{-1}, and for the ferrocyanide it was 2.6 x 10^{-3} mol g^{-1}, determined by atomic absorption.

The cyclic voltammogram of the freshly prepared ferricyanide complex adsorbed on the chitosan surface and that of the free ferricyanide complex are show in Fig. 2. The corresponding and electrochemical parameters are shown in Table 1. The half-wave potential, $E_{1/2}$, for the coupled Fe(II/III) of the ferrocyanide adsorbed on the polymer is 245 mV, and the potential for the free ferrocyanide is 205 mV, both measured against the reference electrode. The interaction between the cyanides of the complex and the hydroxyls of chitosan by hydrogen bonding reduced the δ donor ability of the cyanides, increasing the effective nuclear charge of the metallic center, shifting the oxidation potential to more positive values.

Figure 3A shows the dependence of the current on the intensity with the scan rate. The ratio between the anodic (i_{pa}) and the cathodic (i_{pc}) peak currents is near unity (Table 1), characteristic of a reversible system. Linearity of the anodic current versus the square root of the scan rate (Fig. 3B, plot I_{pa} *vs.* $v^{1/2}$) was also observed, with a correlation coefficient of 0.994, the linearity of these plots indicating the diffusion limitation of the currents within the range of

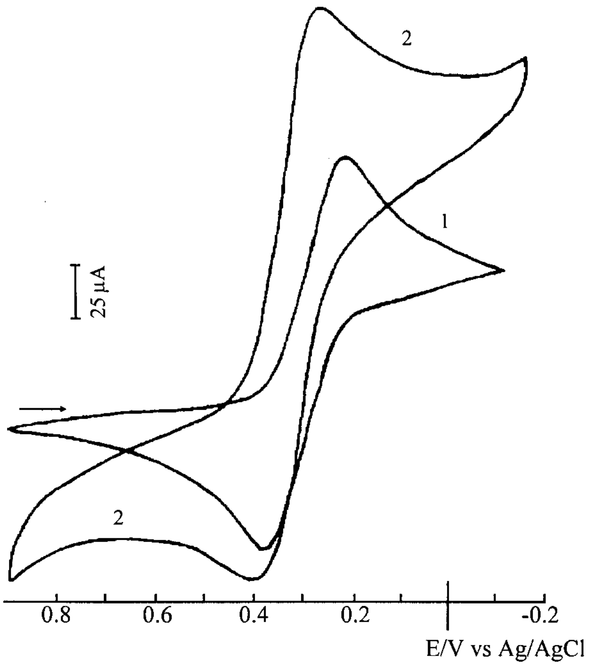

Figure 2. Cyclic voltammograms of (1) ferrocyanide adsorbed on the chitosan surface, and (2) free ferricyanide. In KCl 0.1 M, at pH 3.0, and at a scanning rate of 100 mV s^{-1}.

Table 1. Electrochemical parameters for the ferricyanide and ferrocyanide complexes adsorbed on the QTS surface.

Parameters	$QTS[Fe(CN)_6]^{3-}$	$QTS[Fe(CN)_6]^{4-}$
E_{pc} (mV)	190	180
E_{pa} (mV)	300	310
ΔE_p (mV)	110	130
$E_{1/2}$ (mV)	245	245
I_{pa} (mA)	4.1	1.5
I_{pc} (mA)	4.3	1.8
I_{pa}/I_{pc}	0.95	0.83

the scan rates investigated[13]. The great difference between the anodic and catodic peak potentials, ΔE_p, is attributed to the IR drop in the ferricyanide immobilized on the polymeric matrix[13,12]. The slight displacement of $E_{1/2}$ due to its scanning rate shows that the kinetic of the transfer process is quite fast in this case[14].

Figure 4 shows the voltammogram of the ferrocyanide and ferricyanide complex adsorbed on the chitosan surface, with the electrochemical parameters shown in Table 1. Figure 5 shows a voltammogram of ferricyanide adsorbed on the chitosan surface after exposure to sunlight. The broadening of the oxidation and reduction peaks, as well as the displacement of the $E_{1/2}$ value indicate the presence of more than one species on the polymer surface. The voltammogram of the ferrocyanide species adsorbed on the chitosan does not undergo any change when submitted to sunlight radiation.

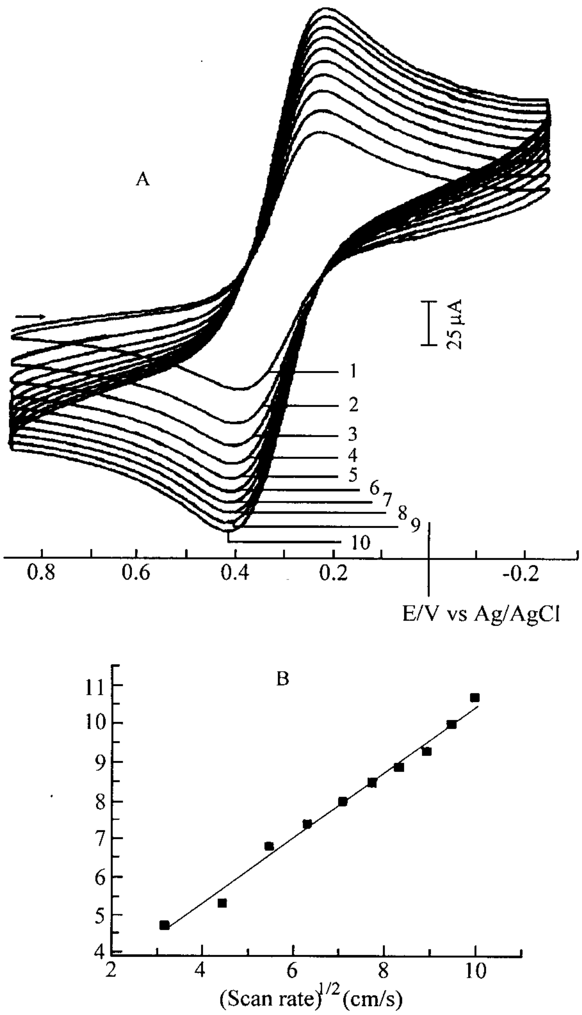

Figure 3. (A) Cyclic voltammograms of ferrocyanide adsorbed on the chitosan surface obtained at different scanning rates: (1) 10 mV s^{-1}, (2) 20 mV s^{-1}, (3) 30 mV s^{-1}, (4) 40 mV s^{-1}, (5) 50 mV s^{-1}, (6) 60 mV s^{-1}, (7) 70 mV s^{-1}, (8) 80 mV s^{-1}, (9) 90 mV s^{-1}, and (10) 100 mV s^{-1} in KCl 0.1M at pH 3.0. (B) The anodic peak current against the square root of the scan rate.

The infrared spectrum of ferricyanide adsorbed on the polymer shows a band at 2114 cm^{-1}, attributed to the CN stretching frequency[15] (Fig. 6A). This band is in the same region as that of the free ferricyanide, indicating that the adsorption of the complex with the chitosan surface is of an electrostatic nature. A stronger interaction would displace the CN stretching band to higher energy regions[16,17]. When the polymer was submitted to sunlight, the appearance of a new band at 2039 cm^{-1} was observed, which has been attributed to the ferrocyanide species[18]. The appearance of this new band is accompanied by the disappearance of the band at 2114 cm^{-1} (Fig. 6B), indicating that the photoinductive reduction process is operating. The infrared spectrum of the ferrocyanide adsorbed on the polymer

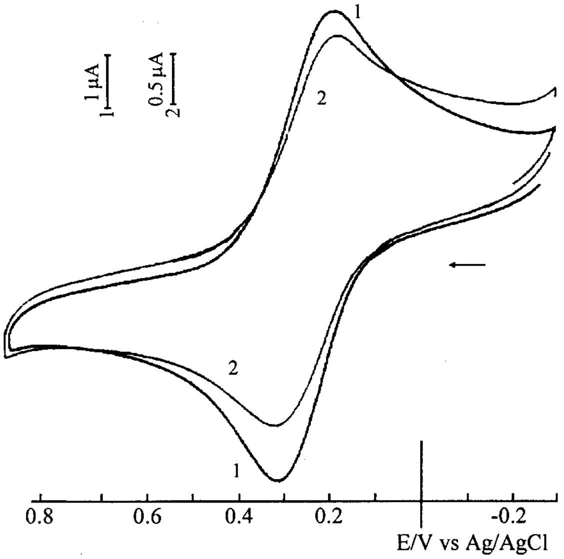

Figure 4. Cyclic voltammograms of (1) the ferricyanide species, and (2) ferricyanide, on the chitosan surface after exposure to sunlight radiation, in KCl 0.1 M, at pH 3.0, and at a scan rate of 100 mV s^{-1}.

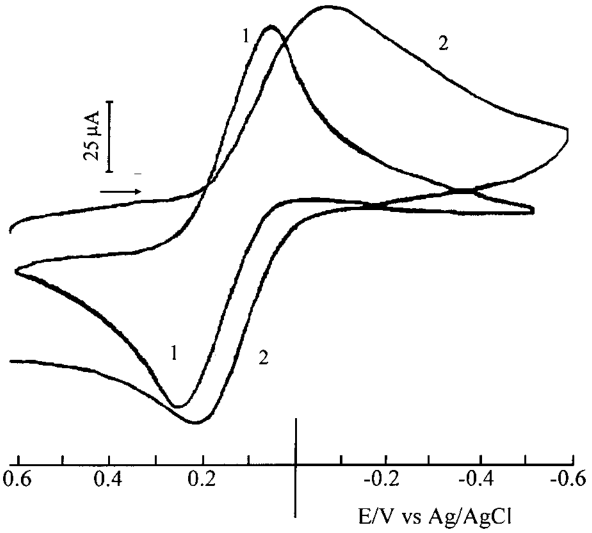

Figure 5. Ferrocyanide adsorbed on the chitosan surface, in KCl 0.1 M, at pH 3.0, and at a scan rate of 100 mV s^{-1}.

shows a band at 2035 cm^{-1} (Fig. 6C), situated in the same region as that of free ferrocyanide[13].

In order to confirm the presence of the species found on the polymer surface using the technique cited above, Mössbauer spectroscopy was also used. Figure 7A shows the Gaussian deconvoluted Mössbauer peaks for the polymer prepared with ferricyanide and submitted to sunlight radiation. In this figure, the most intense peak shows an isomer shift (δ) of -0.03 mm s^{-1}, attributed to the ferrocyanide species adsorbed on the polymer (Figure 7A(b)). The measured δ are in good agreement with of the free ferrocyanide species (-0.04 mm s^{-1}), as show in Fig. 7B.

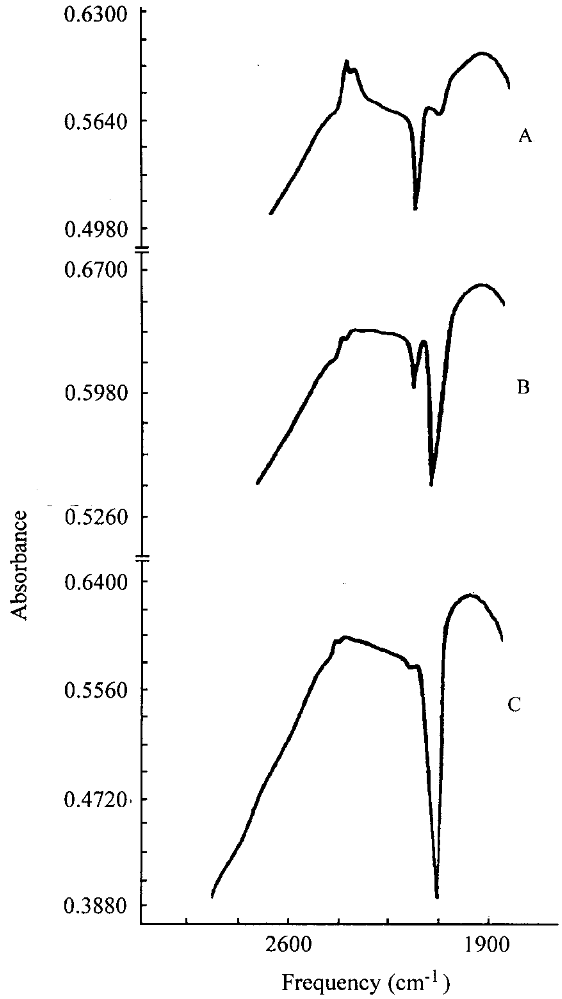

Figure 6. The infrared spectra. (A) ferricyanide adsorbed on the recently prepared polymer surface sample, (B) irradiated sample, and (C) ferrocyanide on the chitosan surface.

Figure 7A(a) also shows that the ferricyanide species adsorbed on the polymer surface, with δ of -0.07 mm s^{-1} and a quadrupole splitting Δ of 0.36 mm s^{-1}, are in good agreement with the free ferricyanide species, (δ of -0.11 mm s^{-1} and a Δ of 0.28 mm s^{-1}), Fig. 7C.

Figure 7A(c) shows the presence of a third species with (δ) of 0.06 mm s^{-1} and a (Δ) of 0.80 mm s^{-1}, which can be attributed to the species $[Fe(CN)_5H_2O]^{3-}$ adsorbed on chitosan[18,19]. These values are very close to those for the same free species, (δ) 0.06 mm s^{-1} and (Δ) 0.79 mm s^{-1}. These data confirm the fact that total conversion of ferricyanide to ferrocyanide does not occur, according to the results showed by the infrared spectra.

A possible decomposition of the redox polymer for the formation of the Prussian and Turnbull blue species on the polymer surface are discarded when compared with the data from the Mössbauer spectroscopy and electrochemical data in the literature[13,20].

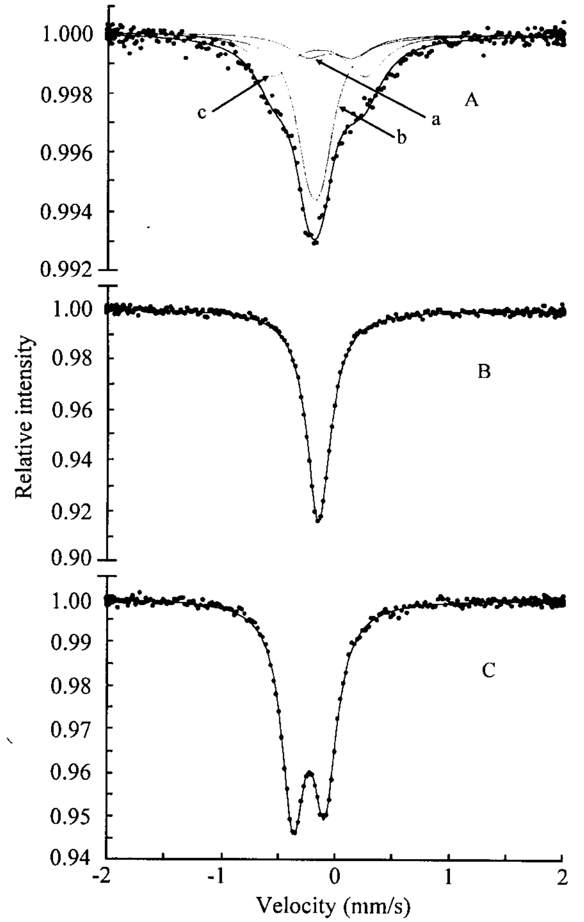

Figure 7. Deconvoluted Mössbauer spectra of (A) ferricyanide submitted to sunlight radiation; (a) ferricyanide, (b) ferrocyanide, and (c) the $[Fe(CN)_5H_2O]^{3-}$ species, (B) free ferrocyanide, and (C) free ferricyanide.

The reduction of ferricyanide to ferrocyanide ocurrs only when the sample is exposed to sunlight. The reduction of ferricyanide complexes to ferrocyanide was also observed by Clearfied and co-workers in zirconium polyimine phosphonates[21]. The photo induced reduction process of the ferricyanide complex on the chitosan surface can be explained by the mechanism of energy transfer in the polymer. This means that it occurs between the donor and receiver electron species in different molecules (intermolecular interactions) or between donor and acceptor groups in the same polymeric chain (intramolecular interactions). Assuming that when chitosan is submitted to sunlight radiation, aminic nitrogen adsorbs a photon and is promoted into an excited state, the electron is later transferred to ferricyanide through a mechanism of intramolecular transfer. Since the polymer is flexible, collisions may occur between the donor groups (nitrogens) and the acceptor (ferricyanides) of the same polymeric chain, reducing ferricyanide to ferrocyanide[22]. The photoinductive reduction mechanism is a remarkable controversy in the literature[1,19,23], although it is of fundamental importance to understand it. Many reactions on the polymer surfaces have important implications: these processes are important in explaining the deterioration of materials in catalytic industrial processes and the phenomena of photographic images.

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