Talanta 154 (2016) 374–380

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Usefulness of palladium impregnated magnetite nanoparticles for polyphenol determination

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ARTICLE INFO

Article history:
Received 27 December 2015
Received in revised form
17 March 2016
Accepted 21 March 2016
Available online 22 March 2016

Keywords:
Polyphenols
Magnetic palladium nanoparticles
Indocyanine green
Fluorometric detection
Wine analysis

ABSTRACT

Palladium impregnated magnetite nanoparticles (Pd-Fe_3O_4NPs) have been synthesized and used as reusable catalyst for the fluorometric determination of polyphenols in wines. The method is based on the decrease of the indocyanine green fluorescence, which is ascribed to its oxidation by dissolved oxygen in the presence of the nanoparticles, and the inhibition of the fluorescence decrease by polyphenols, which is proportional to the polyphenol concentration.

The dynamic range of the calibration graph is 0.1–10.0 μM gallic acid, which was chosen as model analyte, and the detection limit is 0.02 μM. Precision data, expressed as relative standard deviation, ranged between 3.3% and 5.4%. The method was applied to the analysis of several wine samples, obtaining recovery values in the range of 79.7–102.0%. The results obtained were compared with those obtained using the Folin-Ciocalteu and laccase methods, finding that Pd-Fe_3O_4NPs provide a better selectivity than the first method and show a catalytic behavior similar to that of laccase.

1. Introduction

The use of palladium nanoparticles (PdNPs) in chemical processes developed in modern organic chemistry has been widely described. Among other applications, PdNPs are used in catalysis for organic coupling reactions, hydrogenation of unsaturated olefins and oxidation of alcohols and their derivatives [1]. PdNPs have found also a wide application for the development of electroanalytical methods in which these NPs deposited on the electrode surface enhance the performance of the electrode due to their unusual physical and chemical properties, such as biocompatibility, large effective surface area and remarkable electrocatalytic activities [2]. PdNPs-modified electrodes have been used as amperometric sensors for the nonenzymatic determination of hydrogen peroxide [3] and glucose [4–6], avoiding the use of complicated enzyme immobilization procedures and improving the stability of the enzymatic electrodes, which usually is low owing to the intrinsic nature of the enzymes. Similar amperometric sensors have been described for the determination of hydrazine [7], nitrite [8] and catechol [9]. Also, the simultaneous determination of ascorbic acid, dopamine and uric acid has been reported using PdNPs in modified electrodes with carbon nanofibers [10] or multiwalled carbon nanotubes [2].

The catalytic properties of PdNPs have been also exploited for the development of several immunoassays, using electrochemiluminescence [11,12], fluorescence [13] or absorbance [14] measurements, for the determination of α-1-fetoprotein [11,14], thyroid stimulating hormone [12] and human chorionic gonadotropin [13]. The use of PdNPs as labels or solid supports of the antibodies in these immunoassays, improves the analytical signals, reaching very low detection limits.

Polyphenols are a large group of compounds present in a variety of fruits and beverages, such as wine and tea, which help to prevent an array of health problems, including cancer, diabetes, cardiovascular and neurodegenerative diseases, mainly owing to their antioxidant and antiradical activities. Although a high number of chromatographic methods have been described for the identification and quantification of individual polyphenols in food samples, more or less selective methods toward the determination of total polyphenolic content, which are based on their reducing properties, are often used to quantify these compounds in food samples. The photometric Folin-Ciocalteu method [15,16] is frequently used for total phenolic content determination in wines, although non-phenolic reducing compounds, such as ascorbic acid, and reducing sugars interfere the polyphenol determination. More selective methods are based on the use of laccase, which catalyzes the oxidation of polyphenols by dissolved oxygen. Several amperometric sensors based on the use of laccase-modified electrodes have been described [17–19]. These sensors have been satisfactorily applied to the analysis of wines, but they show a

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http://dx.doi.org/10.1016/j.talanta.2016.03.073
0039-9140/

limited lifetime, which is ascribed to the adsorption of oxidized products on the surface of the electrode, affecting negatively the enzyme activity. Laccase has been also used in an automatic method for the determination of polyphenols in wines which involves the use of the fluorophore 8-hydroxypyrene-1,3,6-trisulphonate (HPTS) as substrate and terbium oxide nanoparticles as laccase activator [20].

In this work, the catalytic effect of palladium on the oxidation of polyphenols has been studied with the aim of developing a method for the determination of these compounds in wine, which avoids the relatively high cost of laccase and improves the selectivity of Folin-Ciocalteu method. As the cost of palladium is also relatively high, palladium impregnated magnetite nanoparticles (Pd-Fe_3O_4NPs) have been used, which allows their reusability using an external magnet. The usefulness of these NPs has been described in several organic synthesis reactions [21–23] but, to the best of our knowledge, they have not been used for analytical purposes. This study has been carried out using the long wavelength fluorophore indocyanine green, which is oxidized by dissolved oxygen in the presence of Pd-Fe_3O_4NPs, which results in a fast decrease in the fluorescence. The presence of a polyphenol in the system, such as gallic acid or catechol, slows down the rate of fluorophore oxidation, this effect being proportional to the polyphenol concentration. The results obtained by applying this approach to the analysis of wine samples have been compared with those obtained using the Folin-Ciocalteu [15] and the laccase [20] methods.

2. Experimental

2.1. Instrumentation

A Fluorolog®-3 spectrofluorometer (HORIBA Scientific, New Jersey, USA) equipped with double- grating excitation and emission monochromators, a 450-W Xe light source and a R928P photomultiplier tube was used to obtain fluorometric measurements. Photometric measurements of the Folin-Ciocalteu method were performed using a Lambda 35 UV/VIS spectrometer (Perkin-Elmer, UK).

Nanoparticle characterization was performed by transmission electron microscopy (TEM), using a JEOL JEM 1400. X-ray photoelectron spectroscopy (XPS) data were recorded on pills (10 mm diameter and 0.5 mm thickness) obtained by gently pressing the powdered materials. The main chamber of the Leibold-Heraeus LHS10 spectrometer used, capable of operating down to less than 2×10^{-9} Torr, was equipped with an EA-200MCD hemispherical electron analyser.

2.2. Reagents

All reagents used were of analytical grade. Indocyanine green, 8-hydroxpyrene-1,3,6-trisulphonic acid trisodium salt (HPTS), 2-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (2-Di-1-ASP) and 2-[4-(dymethylaminophenyl]-1,3-butandienyl)-3-ethylbenzothiazolium p-toluenesulphonate salt (Styryl 7) were provided by Sigma-Aldrich (St. Louis, Mo, USA). The synthesis of nanoparticles was performed with urea, iron(II) sulfate heptahydrate and palladium (II) chloride from Sigma-Aldrich and iron(III) chloride hexahydrate and potassium chloride from Panreac (Barcelona, Spain). Di-potassium hydrogen phosphate, tris(hydroxymethyl)-aminomethane (TRIS), sodium hydroxide, hydrochloric acid, sodium sulfite and citric acid were purchased by Merck (Darmstadt, Germany) while hydrogen peroxide was acquired from Panreac. Sodium carbonate, gallic acid, catechol, pyrogallol, ascorbic acid, glucose, malic acid, Folin-Ciocalteu phenol reagent, 2-(N-morpholino)ethanosulfonic acid (MES), sodium dodecyl sulfate (SDS), Triton X-100 and cetyltrimethyl ammonium bromide (CTAB) were also purchased from Sigma-Aldrich.

MES buffer solution (0.2 M, pH 6.0) was prepared by dissolving an appropriate amount of MES in deionized water and adjusting the pH with sodium hydroxide. A 5 mM stock solution of indocyanine green was prepared dissolving the appropriate amount of the fluorophore in dimethyl sulfoxide (Sigma) by sonication for several seconds and stored at room temperature in the dark. Working solutions (25 μM) of the fluorophore were prepared daily by diluting the appropriate volume of the stock solution in the MES buffer solution. A 12 mM stock solution of gallic acid was prepared daily by dissolving the appropriate amount of this polyphenol in deionized water and the different standard solutions were prepared diluting the appropriate volume of the stock solution in the MES buffer solution. A 25 mg mL^{-1} stock Pd-Fe_3O_4NPs dispersion was prepared daily by dispersing the appropriate amount of nanopowder in ultrapure water by using an ultrasonic bath. Aqueous solutions were prepared using ultrapure water purified with a Milli-Q system (Millipore, Bedford, MA, USA).

2.3. Procedures

2.3.1. Synthesis of palladium impregnated magnetite nanoparticles (Pd-Fe_3O_4NPs)

The procedure used to synthesize Pd-Fe_3O_4NPs is similar to those previously reported [21–23]. Briefly, 0.03 mol of $FeCl_3 \cdot 6H_2O$ and 0.06 mol of urea were dissolved in 200 mL of deionized water at 90 °C for 2 h. The reaction mixture, which turned brown, was cooled to room temperature and mixed with 0.01 mol of $FeSO_4 \cdot 7H_2O$. Then, 1 M NaOH was added until pH 10. The molar ratio Fe(III) to Fe(II) was nearly 2.0. The obtained hydroxides were sonicated in a sealed flask at 30 °C for 30 min. After ageing for 5 h, the obtained black powder (Fe_3O_4) was washed and dried under vacuum. After this time, 2 g of Fe_3O_4NPs, 0.2 g of $PdCl_2$ and 0.5 g of KCl were stirred at room temperature in 50 mL of ultrapure water for 1 h. The pH of the suspension was adjusted to 13 by adding 1 M NaOH dropwise, and it was further stirred for 20 h. The solid obtained was washed several times with deionized water and sonicated for 10 min. Finally, the NPs were again washed with deionized water and subsequently with ethanol, and finally dried under vacuum at 60 °C for 24 h.

2.3.2. Determination of polyphenols using the indocyanine green-Pd-Fe_3O_4NPs system

A volume (250 μL) of zero standard, gallic acid standards (0.2–10 μM) or diluted wine sample was added to a 5 mL flask together with 250 μL of 25 μM of indocyanine green and 50 μL of 25 mg mL^{-1} Pd-Fe_3O_4NPs. The flask was raised up to 5 mL with 0.2 M MES buffer solution (pH 6.0). This mixture was homogenized and transferred to a quartz cell, which was immediately inserted in the spectrofluorometer. The variation of the indocyanine green fluorescence intensity with time was monitored for 30 s, using excitation and emission wavelengths of 765 and 800 nm, respectively. Normalized kinetic curves were obtained by dividing the fluorescence signals obtained at each time by the fluorescence signal obtained at time zero for each curve. These curves were treated using Origin software to obtain the reaction rate values and, then, the net reaction rate for each standard or sample, which was the analytical parameter, was calculated by subtracting the reaction rate value of the blank from that obtained for each standard or sample.

2.3.3. Analysis of wine samples

Red and white wine samples were bought at a local supermarket and analyzed immediately after they were opened.