



Voltammetric determination of hydrogen peroxide at high concentration level using a copper electrode



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ARTICLE INFO

Article history:

Received 16 September 2015

Received in revised form 24 November 2015

Accepted 26 November 2015

Available online 28 November 2015

Keywords:

hydrogen peroxide
copper
wastewater

ABSTRACT

The determination of strong oxidizing species is of utmost importance in a number of practical applications. However, the currently available analytical tools should be improved in terms of reliability, automation, and costs. With this respect amperometric techniques are particularly promising candidates; nevertheless, the performance of conventional electrode materials, such as Au and Pt, are unsatisfactory, particularly in terms of resistance to fouling. In addition, electroanalytical methods and devices most commonly pay highest attention to the determination of similar analytes present in trace. On the other hand, the determination of high concentrations is of particular importance in industrial and environmental frames. Especially with reference to similar situations, the present paper reports the electrochemical behavior and analytical effectiveness of an alternative electrode material, namely Cu, in the presence of H₂O₂ at high concentrations (up to 0.5 M) and at different pH values. Furthermore, the behavior in real, harsh matrices, namely wastewater samples exhibiting different levels of chemical oxygen demand, is also reported. The results have been fruitfully employed in the development of an analytical procedure for the determination of H₂O₂ in similar matrices. A statistical treatment of the electrochemical responses suggests that the repeatability and reproducibility are well adequate.

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1. Introduction

Strong oxidizing species are chemicals used in a wide number of laboratory and industrial applications: synthesis of inorganics and organics, treatment of drinking and waste waters, bleaching of cellulose pulp and textile, etc. [1]. As a consequence, the determination of strong oxidants in different matrices, over a wide concentration range, from less than 1 mM to over 10% w/w, constitutes an analytical issue to face under many different conditions. Some recent reviews summarise the literature reports dealing with the determination of H₂O₂ [2–5]. The most common titrimetric and spectroscopic methods are reported in Table S1 in the Supporting Information; they are commonly employed for off- and at-line analytical approaches. It is evident from the literature that many conventional methods cannot be employed when the concentration of oxidisable species is high, as in the case of wastewater samples investigated in the present manuscript. In

particular potassium permanganate or ceric sulphate, commonly used in titration procedures, easily oxidise the organic matter, leading to a significant overestimation of the H₂O₂ concentration. As to spectrophotometric methods, dispersed particulate is present in many samples; in addition, the absorption of many samples due to dissolved species occurs over a broad wavelength range and varies from sample to sample. These drawbacks lead to poor accuracy.

In principle, the electroanalytical procedures may be adapted to work on-line and even in-line [2–7]; however, it often happens that most widely used electrode materials, such as Pt, Au, and glassy carbon (GC), are unsuitable to meet with the request of reliable and repeatable signals. Poisoning irreversible adsorption, leading to fouling of the electrode surface [8], in fact, are most often operative; as a further drawback, different sources of overvoltage [9] may affect the charge transfer, making the relevant responses hidden by the solvent discharge or overlapped to signals due to other reducible species present in solution [10].

The electrode mechanisms involving H₂O₂ cathodic reduction have been investigated on different electrodes; they result in all cases particularly complex and reliable definitive conclusions cannot be drawn out [11–14]. On the other hand, we ourselves

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could check that Pt and GC electrodes cannot be fruitfully employed in the determination of H_2O_2 at high concentration levels [11,12]. *A fortiori*, due to heavy fouling of the surface, Au cannot be employed in real matrices, specifically in those taken into consideration in the present paper. In order to minimise the effect of the fouling different approaches have been adopted, such as digestion of the sample using strong acids; however, they are often impractical in the routine laboratory activity [2–5]. In addition, many electrode systems employ a membrane [2–5]; membranes are mechanically fragile, require the solution to flow on, above a certain flux threshold, and may suffer from clogging.

Once shifting to alternative electrode materials, in particular to unusual metals, Cu-based electrodes deserve attention. Similar electrode systems have been employed in electroanalysis for the amperometric determination of inorganic and organic species such as nitrite [15,16] and carbohydrates [17–19]; both bare Cu electrodes and hybrid electrode coatings containing Cu-based micro and nano-structures, or even Cu coordination compounds, have been reported [20]. In the case of H_2O_2 as the analyte, literature reports mostly the use of CuO_x nanostructures for the determination of low concentration values (<10 mM) [21,22], in the frame of analytical problems quite different from those studied by us (Table S2 in the Supporting Information outlines the most significant literature reports).

On the other hand, the nature itself of the Cu species formed at the surface of the Cu electrode in contact with solutions containing H_2O_2 , both at open circuit and under polarization, is far from being established. Information could be obtained from the studies on the interaction between H_2O_2 and Cu in the frame of corrosion phenomena [23,24] and of chemical-mechanical planarization processes typical of electronic industry [25]. However, the experimental conditions adopted are very different from those suitable to electroanalytical applications.

In the present study voltammetric investigations on the behavior of a very simple electrode system based on Cu, namely bulk Cu, in respect to reduction of H_2O_2 at high concentrations have been carried out. For the choice of optimal experimental parameters, as well as in order to draw calibration plots at different pH values, cyclic voltammetric (CV) responses have been exploited; regression surfaces accounting for the responses of the system at varying the parameters identified as the most meaningful ones, have been accordingly constructed.

Due to the lack of studies using Cu metal as the working electrode under our experimental conditions, the investigation had to start by considering the analyte in 'pure' buffered aqueous solutions. Subsequently, the studies have been extended to real, definitely harsh matrices, namely wastewater samples. Similar fluids have been chosen as meaningful industrial raw sewage: in plants for wastewater treatment, in fact, H_2O_2 is added in order to oxidize dissolved organic species. The pH values and H_2O_2 concentration range have been selected by us taking into account the experimental conditions typical of one of the most widespread methods for wastewater treatment. An effective monitoring of the concentration of H_2O_2 leads to an optimization of the treatment and, consequently, to the saving of energy and chemicals. Wastewater samples constitute a challenging benchmark to ascertain the effectiveness of the system developed. They constitute, in fact, particularly complex matrices, containing a number of potentially interfering and even non-electroactive species, that are possible sources of electrode fouling preventing from obtaining reliable results.

In the case both of buffered aqueous solutions and of the real matrices a suitable experimental design has been drawn and adopted in order to minimize and optimize, at the same time, the experimental effort. The results obtained have been subjected to proper statistical treatment.

The electrode surface has been characterized using Scanning Electron Microscopy (SEM) and Raman spectroscopy, in order to give a structural rationale to the electrochemical behavior.

2. Experimental section

2.1. Chemicals

Chemicals were from Sigma, except for H_2O_2 (40% w/v), which was a Carlo Erba product. The solvent media for the electrochemical investigations were aqueous solutions, at pH buffered between 3 and 7 thanks to citric acid, trisodium citrate dihydrate, acetic acid (99.8% w/w), sodium acetate, NaH_2PO_4 and Na_2HPO_4 . Wastewater samples have been supplied by different companies from Modena district (Italy).

2.2. Procedures

The electrochemical measurements were performed with an Autolab PGSTAT12 (Ecochemie) potentiostat/galvanostat, in single-compartment three-electrode cell, at room temperature. Two-millimeter-diameter Cu disks (99.99% purity) constituted the working electrodes. They were polished subsequently with 1, 0.3, and 0.05 μm alumina powder and then rinsed with Millipore water. An aqueous saturated calomel electrode, KCl sat. (Amel), was the reference electrode; all the potential values given are referred to it. A graphite rod was the auxiliary electrode.

Current/potential curves obtained by CV technique have been recorded at 50 mV/s potential scan rate. The solution has been stirred for one minute between two subsequent potential sweeps, the working electrode being at Open Circuit Potential (OCP).

Fenton reaction [26–28], on which the most widely diffused procedures for determination of H_2O_2 are based, has been carried out by adding H_2O_2 aliquots from 40% w/v stock solution, and solid $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ salt, to wastewater sample. The pH value of these samples has been corrected by addition of solid citric acid and trisodium citrate dihydrate. The influence of the presence of citrate ions on the removal of oxidizable organic species through Fenton reaction has been reported previously [29]: dissolved citrate ions do not dramatically alter the reaction course.

The concentrations of H_2O_2 in the solution taken as the reference for the subsequent measurements, both in buffered media and in wastewater samples, have been determined through standard titration procedure, namely by ASTM D2180 test [30]. The H_2O_2 concentration in the samples does not change during the time length necessary to acquire the voltammetric responses. Similarly, the solution pH is unaltered by the addition of H_2O_2 , even at the highest concentration levels; this holds both for the buffered solutions and for the wastewater samples.

2.3. Experimental design

The dependence of the electrochemical response of Cu electrode on pH and H_2O_2 concentration constitutes a bivariate problem. An almost rotatable and orthogonal inscribed central composite design (CCD) [31,32] has been selected, since it represents a satisfactory compromise between the number of measures to collect and the statistical significance of the resulting response surface—see Supporting Information for more details.

The CV responses at varying pH and analyte concentration have been recorded by randomly changing these independent variables. The adopted regression procedure makes use of a full second order equation (Equation 1), i.e., comprising linear, quadratic, and mixed terms:

$$Q = A \times \text{pH}^2 + B [\text{H}_2\text{O}_2]^2 + C \times \text{pH} + D \times [\text{H}_2\text{O}_2] + E \times \text{pH} \times [\text{H}_2\text{O}_2] + F$$

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