

Determination of the chemical oxygen demand (COD) using a copper electrode: a clean alternative method

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Received: 18 October 2007 / Accepted: 6 May 2008 / Published online: 12 June 2008
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Abstract A clean alternative method for the determination of chemical oxygen demand (COD) was developed using a copper electrode as an electrocatalytic sensor. The measuring principle is based on oxidation current of organic compounds in the wastewater. The effects of important experimental conditions, such as electrolytic solution concentration and potential scan rate, on analytical performance have been investigated. Analytical linear range of 53.0–2,801.4 mg l⁻¹ COD with detection limit of 20.3 mg l⁻¹ COD was achieved. The procedure was successfully applied to the COD determination in wastewater from soft industries. The results obtained using the proposed method were in good agreement with those obtained using the conventional (i.e., dichromate) COD method. In this fashion, the COD value of a sample can be determined in a simple, rapid, accurate manner, and the end products do not contain toxic metals.

Keywords COD · Copper electrode ·
Voltammetric determination · Green chemistry

Introduction

Chemical oxygen demand (COD) is a widely used parameter in controlling the degree of pollution in water

and managing effluent quality. The conventional method for COD determination [1] is defined as the number of oxygen equivalents consumed in the oxidation of organic compounds by strong oxidizing agents such as dichromate and permanganate. However, this method requires the time-consuming process of refluxing samples to achieve more complete oxidation; reproducibility of the results are dependent upon the skill of the operator and expensive (Ag₂SO₄) and toxic (HgSO₄) reagents. Thus, many efforts have been made to solve these problems, but most have entailed automated or simplified versions of the conventional methods [2–5].

In recent years, great deal of effort has been devoted to the development of rapid new methods for the determination of COD. All these new developments have been based on either electrocatalytic [6, 7] or photocatalytic [8–11] oxidation principles. In many cases, the direct oxidation of organic species in aqueous solution using metal or carbon electrodes is not possible because high potentials required for the oxidation of organic compounds usually result in the oxidation of water. However, the copper electrode in alkaline media can act as electrocatalysts for the oxidization of organic species such as carbohydrates and amino acids, which are thought to be mainly responsible for the COD [12–15].

Current and future chemists are being trained to design products and processes with an increased awareness for environmental impact. Outreach activities within the green chemistry community highlight the potential for chemistry to solve many of the global environmental challenges we now face. The origins and basis of green chemistry chart a course for achieving environmental and economic prosperity inherent in a sustainable world [16]. Green chemistry involves the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [17].

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The objective of this study was to develop a simple, fast, inexpensive, and safe electrocatalytic sensor for COD. This work describes an electrochemical method for the estimation of COD using a copper electrode with oxidized surface. The technique is based on the measurement of oxidation currents of organic compounds. The electrode was used for the determination of COD in real samples from various locations sources, and the results were compared with those obtained by the standard method [1].

Experimental

Reagents and solutions

All reagents were of analytical reagent grade from Sigma or Merck, and all solutions were prepared using Millipore Milli-Q deionized water. The electrolytic solution of NaOH was evaluated in a large concentration range between 0.05 and 0.5 mol l⁻¹. A 0.10 mol l⁻¹ glucose solution in NaOH medium was used as the COD standard substance (the theoretical COD value is 19,198.8 mg O₂ l⁻¹).

Apparatus

The cyclic voltammetric measurements were carried out with an Autolab PGSTAT-30 (Eco Chimie) controlled by a PC using the GPES software. The measurements were performed in a 15-ml glass cell containing three electrodes: a Cu/CuO electrode with 9.80-mm² apparent area as working electrode, Ag/AgCl (3.0 mol l⁻¹ KCl) as reference electrode, and a platinum wire as auxiliary electrode. All measurements were performed using non-deaerated 0.1 mol l⁻¹ NaOH solution.

Cu/CuO electrode preparation

A copper rod with a diameter of 6.24 mm and length of 10.0 cm was introduced in a glass cylinder with inner diameter of 8.0 mm and was wrapped with epoxy resin. This electrode stayed for 24 h in room temperature to dry. The electrode surface was polished using 400 and 600 mesh emery paper and thoroughly rinsed with distilled water. Electrode pretreatment was done for 15 min in 0.1 mol l⁻¹ NaOH solution with cycling the potential between -1.0 and +0.70 V vs. Ag/AgCl. This massive oxidation resulted in a blackish surface film (formation of copper oxide) on the originally shiny copper surface.

Real water samples

The real samples used in this study were collected within the São Paulo State (São Carlos region) in Brazil from

various sites including wastewater treatment plants and soft drink industries. All samples were preserved according to the guideline of the standard method. After dilution, the samples were simultaneously analyzed by both standard COD method (K₂Cr₂O₇) [1] and voltammetric method. Experiments were performed 1–2 days after sampling. Just before voltammetric experiment, aliquots of the samples were added into the electrochemical cell containing 10.0 ml of NaOH solution. This final solution was finally homogenized with a magnetic stirrer; the cyclic voltammograms were recorded by cycling the potential between 0.25 and 0.90 V vs. Ag/AgCl at a scan rate of 20 mV s⁻¹. A blank solution without addition of sample was used to obtain the base current. No other treatment of the samples was required.

Results and discussion

Voltammetric studies

The metallic copper in alkaline media can electrocatalytically oxidize a wide range of organic compounds mainly responsible for the COD of natural waters. This catalytic action is mediated by surface oxides [18] which are easily formed in ambient air or under anodic conditions [12–15].

Typical current–voltage obtained at the copper electrode in a 0.1 mol l⁻¹ NaOH is illustrated by the cyclic voltammogram shown in Fig. 1. The anodic peak 1 (-0.38 V vs. Ag/AgCl) corresponds to the formation of a first layer of copper(I) oxide (Cu₂O), while the broader anodic peak 2 (-0.11 V vs. Ag/AgCl) corresponds to formation of a second mixed layer of copper(II) oxide/copper(II) hydroxide (CuO/Cu(OH)₂). Reaching 0.70 V vs.

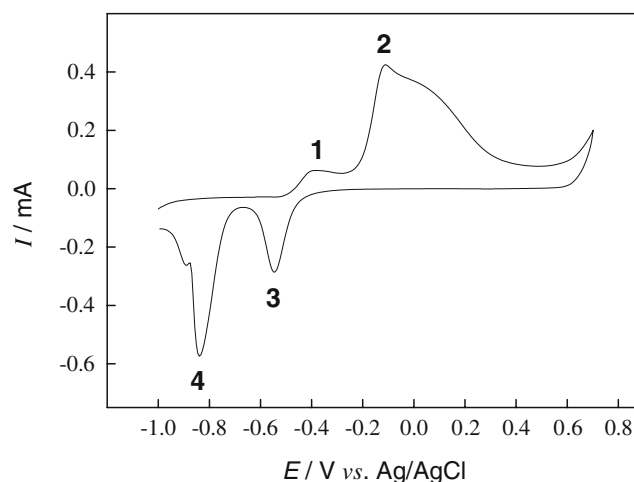


Fig. 1 Cyclic voltammetric response of the metallic copper electrode in 0.1 mol l⁻¹ NaOH solution. Potential scan window, -1.0 to +0.70 V vs. Ag/AgCl (3.0 mol l⁻¹ KCl). Scan rate, 20 mV s⁻¹

Ag/AgCl indicates the Cu(II)/Cu(III) oxidation. Examining reverse scan could reveal the cathodic peaks 3 and 4 corresponding to the Cu(II)/Cu(I) (−0.55 V vs. Ag/AgCl) and Cu(I)/Cu(0) (−0.84 V vs. Ag/AgCl) reduction reactions, respectively. Several studies for the electrooxidation of metallic copper in alkaline media have been carried out using different techniques [19–21]. This electrochemical process is highly dependent on both the hydroxide concentration and the previous formation of a specific layer of Cu(II) oxide [21]. The participation of the Cu(III) species as an electron-transfer mediator has been suggested for explaining the good performance of copper electrodes in alkaline medium in anodic processes related to several organic compounds.

Hydroxide ions are required to neutralize the protons generated during the formation of active sites CuO(OH) through discharge of water. At low hydroxide concentrations, formation of active sites would be expected to proceed at a slower rate, which directly affects the formation of the bridged intermediate [22]. The NaOH concentration effect in the range from 0.05 to 0.5 mol l^{−1} on the anodic peak potential of the Cu/CuO electrode was evaluated. The peak current increased with increasing NaOH concentration up to 0.1 mol l^{−1}. Therefore, a 0.1 mol l^{−1} NaOH solution was selected for further studies due to the best voltammetric profile with peak potential well defined.

Sensor performance for the determination of COD

Glucose was used as an organic compound for further investigations in the determination of COD. Figure 2 shows

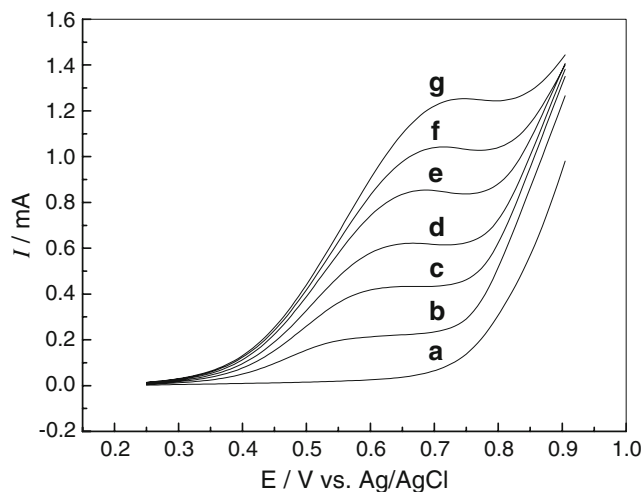


Fig. 2 Linear sweep voltammograms of the copper electrode in 0.1 mol l^{−1} NaOH solution containing concentrations different of organic compound. **a** Absence (background); **b** 2.50; **c** 4.95; **d** 7.4; **e** 9.80; **f** 12.20; and **g** 14.60 mmol l^{−1}. Potential, +0.25 to +0.90 V. Scan rate, 20 mV s^{−1}

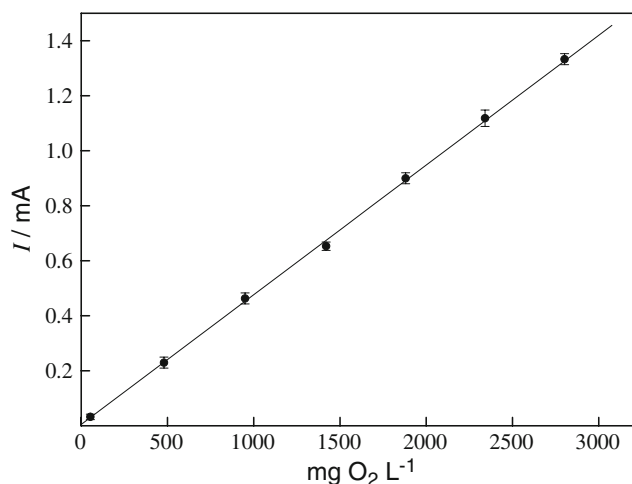
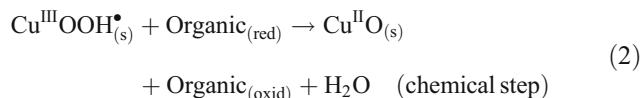
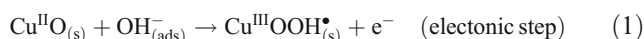


Fig. 3 Calibration plot of current signal, Δ*I*_{pa}, of the copper electrode as a function of COD values. The experimental condition as described in Fig. 2 and substrate was glucose solution. The anodic current measurements was realized in triplicate for COD values

linear sweep voltammograms (with background) acquired from the oxidation of organic compound. It can be seen that the maximum oxidation current of organic compound occurs at 0.70 V (vs. Ag/AgCl) in 0.1 mol l^{−1} NaOH solution. This behavior is typical of that expected for electrocatalytic oxidation as follows [18, 20]:



This agrees with the proposed involvement of copper(II) and copper(III) surface species in the oxidation of organic compound, as Cu(II) and Cu(III) species are present in this potential range [20].

Table 1 Comparison of COD values (mg l^{−1}) obtained by the proposed method with those by standard method [1]

| Samples | COD values (mg l ^{−1}) | | <i>E_r</i> (%) |
|---------|----------------------------------|------------------------------|--------------------------|
| | Standard method ^a | Proposed method ^a | |
| A | 13,010±25 | 12,893±18 | −8.9 |
| B | 16,032±20 | 15,006±12 | −6.4 |
| C | 19,209±23 | 17,800±20 | −7.3 |
| D | 1,740±10 | 1,410±5 | −19 |

E_r relative error = proposed method vs. conventional method

^a Mean of three determinations ± SD

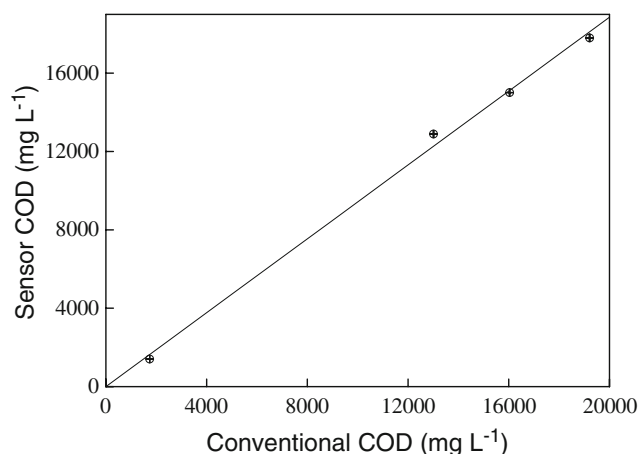
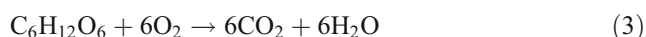


Fig. 4 Relationship between COD of real wastewater samples obtained by the proposed method and the standard COD method

The effect of the scan rate on the voltammetric response of a Cu/CuO electrode in 0.1 mol l⁻¹ NaOH containing 0.1 mol l⁻¹ glucose was studied. When peak current values were plotted against $v^{1/2}$, a linear relationship was obtained. The change of peak current with the scan rate reveals a typical diffusion controlled behavior. From these results, a scan rate of 20 mV s⁻¹ was chosen for the further studies.

Using glucose at various concentrations, a calibration graph was prepared based on the following reaction:



The peak current at 0.70 V increased linearly with the COD value (obtained by theoretical oxidation of glucose; Eq. 3) in the concentration range from 53.0 to 2,801.4 mg l⁻¹ COD (see Fig. 3). The calibration curve was constructed between COD concentration and the current, which was obtained from the difference of background current and the peak height in the presence of organic compound. A linear relationship was found as follow:

$$\Delta I_{\text{pa}}(\text{mA}) = 0.005 + 4.717 \times 10^{-4}[\text{COD}](\text{mg l}^{-1}) \quad (4)$$

$$r = 0.9997$$

where ΔI_{pa} is the corresponding peak anodic current. According to IUPAC, the detection limit was determined by three times the standard deviation from the blank signal (three times the signal blank/slope) as 20.3 mg l⁻¹.

Table 2 Analytical features of different electrochemical sensors for COD determination

| Analytical parameters | Proposed electrode | Boron-doped diamond [23] | F-PbO ₂ modified electrode [24] | Ti/TiO ₂ /PbO ₂ electrode [25] |
|--------------------------------------|--------------------------|--------------------------|--|--|
| L.R. (mg l ⁻¹) | 53.0–2801.4 | 20–9000 | 100–1200 | 20–2,500.0 |
| D.L. (mg l ⁻¹) | 20.3 | 7.5 | 15 | 10 |
| Sensitivity (mA l mg ⁻¹) | 4.717 × 10 ⁻⁴ | 3.8 × 10 ⁻³ | 2.3 × 10 ⁻⁷ | 3.202 × 10 ⁻³ |

L.R. liner range, D.L. detection limit

Determination of COD in real samples

A number of organic compounds considered to have environmental significance were chosen as samples, with the aim of establishing some relationship with the organic species existing in wastewaters. Lee et al. [7] have postulated the oxidation of organic compounds at copper oxide surfaces and have observed that all organic compounds investigated were stoichiometrically oxidized to their highest oxidation form.

Several real samples were collected in different soft drink manufacturers to determine the possibility of applying this sensor to wastewater monitoring in treatment plants. The COD value of the samples were evaluated by standard addition method and compared with that determined by conventional COD method [1]. The results are given in Table 1, which shows that COD values obtained using the proposed method are within ±10% of those given by the conventional COD method. This result indicated that the COD values of real wastewater samples, obtained using the proposed method, are similar to those obtained using standard method. Good recoveries (72–110%) of the standard substance added were obtained. Figure 4 shows the relationship between the results obtained by the proposed and the conventional methods (dichromate) for four wastewater samples, and the correlation was satisfactory. The linear regression equations and correlation coefficient were:

$$\text{COD}(\text{sensor method}) = 0.9429 \times \text{COD}(\text{conventional method})$$

$$r = 0.9982 \quad (5)$$

More importantly, the slope of the principal axis of the correlation of 0.9429 was obtained. This almost unity slope value suggests that both methods were accurately measuring the same COD value.

Conclusion

The objective of this work was to demonstrate the viability of a sensor for chemical oxygen demand using a copper electrode

as electrochemical detector. The main advantage of this electrocatalytic sensor for COD are simplicity of preparation and low cost. In addition, the good stability of the electrode was tested over a 15-day period. On each day, ten measurements using the same surface of the electrode were realized. The time taken to measure one sample was 10–20 min, as compared with 2–4 h using the conventional methods. The electrode response is comparable to the conventional method [1]. Additionally, this method was satisfactory for the COD determination of wastewater samples and is a more environmentally friendly approach to COD determination. Analytical features of several electrochemical sensors for COD determination are presented in Table 2.

Acknowledgments The financial support by FAPESP is gratefully acknowledged. The authors thank SJT.

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