

Electrochemical Assessment of Amperometric Oxidability Level in Water Pollution Monitoring

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Abstract. Three types of electrodes were obtained and characterized in order to use for detection of some electrochemical oxidable organics conventionally considered responsible in COD parameter evaluation: electrodes based on undoped and Co-doped lead dioxide, electrodeposited from slight acidic solutions on stainless steel support; electrodes based on copper/copper oxides obtained *in situ* in alkaline medium by potential cycling between the selected potential values or by polarization to a fixed potential value. The electrochemical and un-electrochemical characterization of the obtained electrode materials was studied. Detection experiments and calibration tests provided information regarding: amperometric detection type, detection potential value, amperometric oxidability level (AOL), electrode sensitivity, concentration ranges, stability, reproducibility of signal, detection limits, and lifetime.

Keywords: wastewaters, COD parameter, electrochemical sensing, copper/copper oxide electrode, amperometric oxidability level, pure and Co-doped lead dioxide electrode

1. Introduction

Water quality management usually involves monitoring a series of key pollutants that serve as indicators of acceptability for a specific use. An important pollutant class for wastewater monitoring is organics, usually involved in a conventional COD (chemical oxygen demand) parameter. A new alternative of unconventional method of the oxidable organics and inorganics evaluation could be electrochemical methods, as AOL (amperometric oxidability level) assessment. AOL index can be expressed as the fast amperometric signal obtained in a certain potential range prior settled based on the voltammogram. This electrochemical method requires appropriate electrode materials types with suitable properties for their use as electrochemical detectors in this task. The electrode materials elaboration, characterization and their use for quantitative evaluation of organic pollutants requires the use of un-electrochemical and electrochemical techniques to study the surface properties and electrochemical activity or availability for use as adequate detectors/sensors.

Three types of electrodes were used for detection of the electrochemical oxidable organics. The used, developed and elaborated electrodes in our work based on copper/copper oxides obtained *in-situ* in alkaline medium by potential cycling between the selected potential values or by polarization to a fixed potential value [1,13-25]; electrodes based on undoped and Co-doped lead dioxide, electrodeposited from slight acidic solution on stainless steel support [1-12];

This paper presents our original results using three types of obtained electrodes for the quantitative evaluation of the following compounds: carbohydrates class (e.g.: glucose, mannose, arabinose, maltose, tartaric acid, ethanol

and glycerin), Sulf- containing organics class (e.g.: thiourea and cysteine) which can be proceeded from food and other industries; Nitrogen -containing organics class (e.g.: cysteine), which are found in biological waste.

2. Experimental

Stainless steel was used as support to deposit films based on PbO₂ (type 1) and Co-doped PbO₂ (type 2). The undoped lead dioxide electrode was obtained by anodic electrodeposition of PbO₂ film on a stainless steel support by electrochemical oxidation from 1M Pb(NO₃)₂ solution. Two variants of Co-doped PbO₂ electrodes were obtained on the stainless steel support by two methods: Variant 1- in galvanostatic condition with a two-electrode system, which consisted of an electromagnetically vibrated working electrode (frequency = 50 Hz) and a cylindrically copper foil with high surface. The electrodeposition time was 10 minutes; Variant 2- in potentiostatic condition, when the potential was fixed to 1.8 V/SCE for duration of 10 minutes. The electrodeposition experiments for variant 2 were carried out using a glass cell equipped with a three-electrode system. This electrode system consisted of: ultrasoned working electrode with area of 0.1256 cm², a platinum plate counter electrode and a SCE (saturated calomel electrode) reference electrode, respectively. The whole glass cell was introduced into the ultrasonic bath. The Co-PbO₂ films were electrodeposited from solutions of lead nitrate and cobalt nitrate. The electrolyte compositions were: 0.5 M Pb(NO₃)₂; 0.2 M Co (NO₃)₂ in variant 1 and 0.5 M Pb(NO₃)₂; 0.5 M Co (NO₃)₂ in variant 2, respectively.

In all situations, stainless steel support was polished with two-degree emery papers, degreased and carefully

rinsed with distilled water before of each electrodeposition experiment.

In order to obtain a fresh copper electrode surface, the copper electrode was polished with alumina powder suspended in distilled water. The alumina powder on the electrode was removed and the electrode carefully washed with double distilled water. The electrode was the immediately used for experiments as a polished fresh copper electrode. The working electrode area was 0.0314 cm². The copper/copper oxides electrodes were preformed by five repeated scanning in a potential range of -0.221V to +1V (first vertex potential) and -1V (second vertex potential), vs. SCE, in the first variant, or by a polarization at constant potential, in the second variant.

Scanning electron microscopy (SEM) (Jeol JSM-5800LV) was used in conjunction with energy-dispersive X-ray spectrometer (EDX) to study the morphology and determine the composition of films. The identification of the phases was performed *ex-situ* by Grazing incidence X-ray diffraction (XRD), using an X-ray diffractometer (Bruker D8 Advance Diffractometer). To determine quantitative composition of Co-doped lead dioxide atomic absorption spectrometry analysis was made, using Varian A110 spectrometer.

The useful data for the amperometric detection of electrochemical oxidable organics were obtained using cyclic voltammetry (CV) and/or chronoamperometry [1]. The voltammetric and chronoamperometric study performed with an potentiostat Autolab PGstat EcoChemie, controlled by a PC running version 4.8 GPES Software. All potentials were expressed versus saturated calomel electrode (SCE), as reference electrode.

All chemicals were of analytical grade reagents, Fluka or Merck products.

3. Results and discussion

Table 1. Elaboration conditions of the electrodes

Electrode type	Support	Working conditions	Bath composition
Copper/copper oxide electrode	Copper wire	Five repeated scanning in a potential range of -0.221V to +1V and to -1V, vs. SCE.	NaOH 0.1 M
Pure lead dioxide electrode	Stainless steel	Potentiostatic conditions (ultrasonic bath) Galvanostatic conditions (vibrating electrode)	Pb(NO ₃) ₂ 1M
Co-doped lead dioxide electrode	Stainless steel	Potentiostatic conditions (ultrasonic bath) Galvanostatic conditions (vibrating electrode)	Pb(NO ₃) ₂ 0.5 M and Co (NO ₃) ₂ 0.2 M; Pb(NO ₃) ₂ 0.5 M and Co (NO ₃) ₂ 0.5 M

The three types of electrodes obtained by the electrochemical pathways from different supporting electrolytes were used for the electrocatalytic oxidation of some electrochemical oxidable organics in order to detect them. A brief characterization of elaboration conditions of the electrodes is gathered in table 1.

The surface morphology and the chemical composition of the films have been examined by the SEM/EDX, XRD, and AAS technique. Pure PbO₂ and Co-doped PbO₂ electrode has a crystalline structure with well-formed crystals, while a copper/copper oxide film is amorphous. The main results are listed in table 2.

Some classes of organic pollutants from wastewater that are thought to be mainly responsible for the COD (chemical oxygen demand) parameter, which are tested for the amperometric detection on both electrode types, are presented in table 3.

Table 2. Data regarding the structural and chemical characterization of the electrode

Electrode type	Characteristics	Used technique
Copper/copper oxide	Amorphous film	SEM/EDX
PbO ₂	Crystalline film α -PbO ₂ and β -PbO ₂ forms	SEM/EDX XRD
Co-doped PbO ₂	Crystalline film, presence of Co in lead dioxide deposit β -PbO ₂ , Co ₃ O ₄ forms Molar ratio of Co/Pb= 0.01-0.029	SEM/EDX XRD AAS

Table 3. Selected organics for the quantitative evaluation and their potential origin

Compound class	Target species	Possible source
Saccharides	Glucose, mannose, galactose, arabinose	Municipal wastewaters, wastewaters proceeded from food and beverage industry, medical waste, biological waste
Alcohols	Ethanol, glycerine	
Carboxylic acids	Tartaric acid	
S-containing organics	Cysteine, thiourea	

From a large series of the obtained electrochemical data [1], a detailed example of the cyclic voltammograms (CVs) on copper/copper oxide electrodes in the presence of different cysteine concentration is presented in figure 1. This figure shows the detail of the cyclic voltammograms obtained for potential range from -1V to +0.75V/SCE for copper oxides formed by five repeated scans in the same range in alkaline medium at increasing concentrations of cysteine. Also, it is shown for comparison, the background cyclic voltammograms obtained under identical conditions but in the absence of analyte (curve 1). For this example, in order to establish the calibration plot there are two ranges of concentrations presented in figure 2 a, b). For the both concentration ranges: 0.2 mM - 2 mM and 2 mM - 6 mM, the linear

relationships were found between the cyclic voltammetric anodic limiting waves and the cysteine concentration at scan rates of 0.05 V/s.

The effect of the scan rate increase on the copper/copper oxide electrode in the presence of organics (e.g. glycerine) is exemplified in the figure 3. Under these conditions, can be assumed that glycerine interacts both with oxide/hydroxide film that affect the film formation during anodic scanning and Cu (II)/Cu (III) couple, which mediate the process in the limiting current range. It can be noticed the cathodic peak trend (especially for higher scan rates) that can be attributed to the reduction of Cu (III) or/and oxidation product of glycerine.

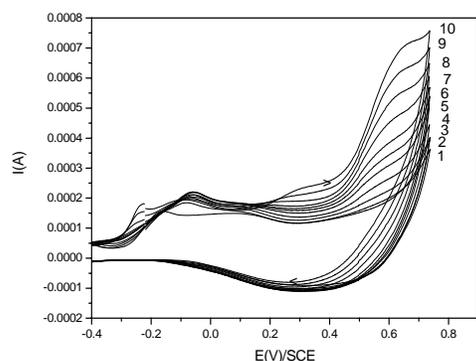


Fig.1. CVs (detail): copper electrode in NaOH 0.1 M, aerated solution; Cysteine:0; 0.2; 0.4; 0.8; 1.2; 1.6; 2-6 mM (curves: 1-10); scan rate: 0.05 V/s; 2nd scan; Potential range: -0.221 V → +0.75 V → -1 V → -0.221 V/SCE; Inset: current value versus cysteine concentration for E = +0.6 V/SCE

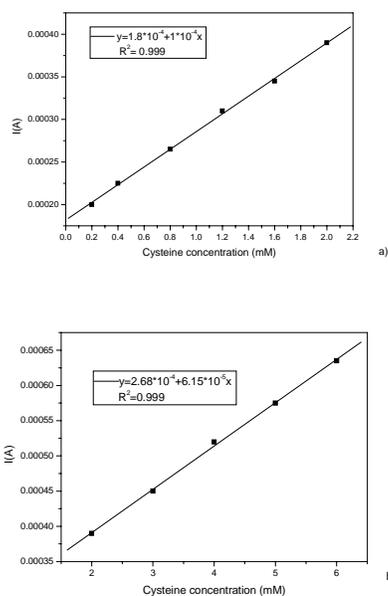


Fig.2. Calibration plot obtained for range of: a) 0.2; 0.4; 0.8; 1.2; 1.6; 2 mM cysteine; b) 2; 3; 4; 5; 6 mM cysteine; E = +0.6 V/SCE

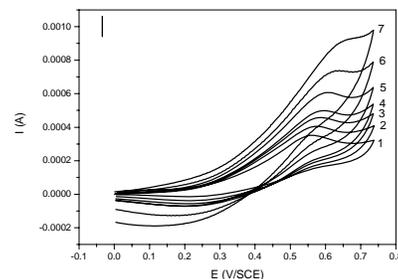


Fig. 3. Cyclic voltammograms: copper oxide electrode performed by 5 consecutive scans in NaOH 0.1 M and tested in glycerine 7 mM; 1-7: scan rate: 0.01, 0.02, 0.03, 0.04, 0.06, 0.1, 0.2 V/s

The results of the detection experiments performance, which provided informations regarding: target species, electrode type, solution type, concentration range, potential range and other observation for the three electrode types and for some electroactive organics are listed in table 4.

For all studied carbohydrates there was a relationship between amperometric signal on copper/copper oxide electrode and organic concentration, and the electrode sensitivity, concentration range are presented in table 5.

Table 4. Amperometric responses on the tested electrodes of some electroactive organics

Target electroactive species	Electrode type	Medium	Concentration range (mM)	Potential range/ selected value (V/SCE)	Observation
Glucose	Copper/copper oxides	alkaline	0-8	+0.3÷+0.7	Stable electrode Good sensitivity
	Co-doped PbO ₂	acidic	0-4	+1.5	Dynamic voltammetric conditions
	Co-doped PbO ₂	alkaline	0-3	+0.5÷+0.65	Low sensitivity
Cysteine	Copper/copper oxides	alkaline	0-6	+0.3÷+0.7	Good sensitivity
	Pure PbO ₂	acidic	0-8	+1.25÷+1.5	Stable electrode
Thiourea	Copper/copper oxide	alkaline	0-8	+0.3÷+0.7	Good sensitivity
	Pure PbO ₂	acidic	0-5	+1.25÷+1.5	Stable electrode

For glucose and tartaric acid, for concentration higher than maximum detection limit (without electrode surface cleaning), electrode fouling occurred. After mechanical cleaning of fouled electrode surface, copper/copper oxide electrode exhibited an amperometric signal that is proportional to the organic concentration.

Table 5. Copper/copper oxide electrode sensitivity for some organics detection for potential value of +0.6 V/SCE

Target species	Electrode sensitivity* (mA/mM)	Concentration range (mM)	Observations
Glucose	0.0546	0-8	Electrode fouling (for glucose concentration > 8 mM)
Galactose	0.0457	0-8	
Arabinose	0.0478	0-8	
Mannose	0.0395	0-8	
Tartaric acid	0.0500	0-6	
Glycerine	0.0478	0-9	Electrode fouling (for tartaric acid concentration > 6 mM)

* Electrode sensitivity corresponds in fact to the normalized AOL conventional parameter/index and reflects the susceptibility of exemplified organics to oxidation. AOL represents the product between sensitivity and concentration, i.e., measured anodic current directly proportional with concentration [1].

In this way, a direct and fast amperometric measurement is available as substitute for the long and more complicated methods which involve the advanced chemical or electrochemical oxidation.

The effect of supporting electrolyte, interferences and the establishment of minim detection limit requires the future research.

Due to the great complexity of the objective proposed for the study, this study was conceived and tackled as a necessary and obligatory stage that to precede the effective implementation of detectors for industrial applications and on-line monitoring of polluted and treated wastewater.

The basic study for detectors elaboration, characterization and use for sensing is a stage that conditions fundamental and hard criteria of „know-how” for concrete application.

4. Conclusions

The three types of elaborated and studied electrodes were proved as electrochemical detectors for various organic compounds.

The structural aspects favoroud the good agreement with the task imposed by amperometric condition. The amperometric data and sensitivity of the detectors are very promising for AOL detection.

The rapidity exploitation, sensitivity and the easy of maintenance of the systems of amperometric detector-cell type, including fast regeneration of fouled or exhausted detectors will be a advantage versus the classical method of COD evaluation. This advantage is due to the fact the

complete oxidation of organics (analyte) is not necessary. This type of detection requires the obtaining of fast and simple response proportional with global concentration, which is the sum of specific component, as electrochemical oxidable substances.

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