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SIMULTANEOUS VOLTAMMETRIC DETECTION OF ORGANICS FROM WASTEWATER ON A COPPER OXIDE-COPPER ELECTRODE

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Abstract

The amperometric response in dynamic or fixed potential conditions, as cyclic voltammetry (CV) and chronoamperometry (CA) of a copper oxide-copper electrode was studied and proposed for the fast characterization of the simulated wastewaters containing acetylsalicylic acid (ASA) and sulfur compounds, i.e., thioacetamide (TA) as organic pollutant models. The additivity of the individual amperometric signals in the overall response of the electrode for mixed solutions corresponded to over 95% recovery degree. Some supplementary considerations on the qualitative and quantitative determination were underlined. The sum amperometric signal could be proposed and used as a easy accessible characterization parameter of organic load from wastewaters and a substituent of classical, time-consuming and poorly recovered COD (chemical oxygen demand). In this way, the copper oxide-copper electrode offered a very cheap support for the practical purposes, e.g., wastewater characterization.

Keywords: copper oxide-copper electrode, organic load, electrochemical detection, voltammetry, chronoamperometry

1. Introduction

The wastewaters resulting from organic synthesis and drug processing contain organic pollutants that require oxygen for their decomposition and may exert negative effects on these environments. These effects can be estimated using either the biological oxygen demand (BOD) concept that is a measure of the biodegradability of pollutants in terms of oxygen required for their decomposition, or chemical oxygen demand (COD) parameter that is often used as a substitute for BOD, and it serves for the purpose of the monitoring organic pollution in water. The conventional methods for COD evaluation require the time-consuming process of refluxing samples (Eaton et al., 1995) and the reproductibility of the results are dependent upon the operator's skills. The amperometric detection of organic load could be used as an alternative for COD evaluation, allowing besides the simultaneous detection of organics the possibility to evaluate selectively of certain pollutants.

In this paper, the thioacetamide (TA) and acetylsalicylic acid (ASA) were chosen as simulated pollutants for wastewater proceeded from organic synthesis and drug processing. Acetylsalicylic acid, popularly known as aspirin is one of the most widely used drug in the world and various analytical techniques for the determination of ASA in biological fluids and pharmaceuticals formulations have been explored, i.e., potentiometry, spectrophotometry, chromatography, voltammetry (Kubota et al., 1999; Ni et al., 2004; Quintino et al., 2002; Torriero et al., 2004). The thioacetamide is well-known representant of the thioamides and its use involves the overall technical availabilities of this class of substances (Manea et al., 2006) and it can be seen as a representative pollutant for sulfur-containing organic class responsible for COD parameter of the corresponding wastewaters. Thioacetamide is used as a sulfur source in various organic compounds synthesis, in leather processing, in laboratories as a substitute for hydrogen sulphide, and other applications, e.g., metal

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ion analysis (Krijn et al., 1960). At the same time, thioacetamide belongs to a class of hepatotoxic thioamidic compounds (thiourea and its derivatives) (Fan and Weng, 2005; Okuyama et al., 2003; Spataru et al., 2001; Theocharis et al., 2000). The electroanalysis of the substances from thioamides series arise serious difficulties and sometimes is imposed distinct circumstances as pulsed amperometric detection (PAD) or cathodic stripping voltammetry (Chailapakul et al., 2003; Lawrence et al., 2002; Spataru et al., 2001), the electrochemical detection of sulfur-containing organics has been yet a opened subject (Lawrence et al., 2002; Manea et al., 2006; Polta and Johnson, 1986; Spataru et al., 2001).

The development of a simple, specific, sensitive and inexpensive method for the simultaneous detection of these compounds regarded as representative pollutants for wastewater could be useful and advantageous. The copper oxide-copper is a very cheap, easy operating and renewable electrode, which offer the large possibilities of amperometric detection of some organics (Luo et al., 1990; Manea et al., 2005; Marioli and Kuwana, 1992).

In this work we developed a simple and direct method for the rapid evaluation of ASA and TA at the copper oxide-copper electrode as the individual and overall detection in aqueous systems. The method regards a qualitative selective evaluation of TA in the presence of ASA and a quantitative assessment of the overall organic load, as cumulative amperometric response. In addition, a correlation between classical determined COD parameter and electrochemical method can be determined.

2. Experimental

The electrochemical measurements were performed in a Metrohm glass cell equipped with a three electrode system, a stationary horizontal copper disk electrode (working electrode) embedded in an insulating Teflon rod, which was fixed in a holder, a platinum foil as a counter electrode, and a SCE (saturated calomel electrode) as a reference electrode. The copper (advanced purity material) disk having diameter of 2.8 mm was used. The supporting electrolyte was 0.1 M NaOH for all measurements. Thioacetamide, acetylsalicylic acid and sodium hydroxide solutions were prepared from analytical grade reagents (Merck) in double distilled water. The working temperature was 22 ± 0.5 °C.

To get a freshly cleaned copper electrode surface, the copper electrode was polished with emery fine paper and alumina powder of 0.25 and 0.1 μm suspended in distilled water, and carefully washed with double distilled water. The freshly cleaned copper electrode was used as a starting material for electrochemical conditioning treatment copper oxide formation and the use as working electrode in the amperometric detection experiments. Prior to use as detector, the copper oxides-copper electrode was preformed in 0.1 M NaOH solution by cyclic repeated scans, e.g. five repeated scans within a potential range

of -0.221 V to $+1$ V (first switch potential) and -1 V (second switch potential) vs. SCE. The supporting electrolyte in the voltammetric and amperometric investigation and detection was 0.1 M NaOH solution. The voltammograms and chronoamperograms were obtained by using an Autolab PGstat 20 EcoChemie system controlled by a PC running 4.8 version of GPES Software.

To evaluate COD parameter, the classical method in according with American standard (Eaton et al., 1995) was used.

3. Results and discussion

3.1. Cyclic voltammetry data

Cyclic voltammetry was used to study the electrochemical oxidation of both target organics at the copper electrode in alkaline solution. The behavior of the copper electrode in 0.1 M NaOH solution and in the presence of ASA and TA was examined by sweeping potential between -1 V to $+0.75$ V vs SCE by repetitive cyclic voltammograms at a scan rate of 0.05 $\text{V}\cdot\text{s}^{-1}$. Fig. 1 shows the cyclic voltammograms obtained at copper electrode in 0.1 M NaOH as supporting electrolyte (curve a), in the presence of 2 mM ASA (curve b) and in the presence of 2 mM TA (curve c). Our results agree well with our previous studies of copper electrodes in alkaline solution, in the presence of carbohydrates (e.g., glucose, sodium urate) (Manea et al., 2005; Manea et al., 2006), and in the presence of sulfur-containing organics (Manea et al., 2006). The anodic peak at -0.4 V vs SCE is typically for thioamides and thioamides-copper complexes, e.g., thiourea, discussed in our previous paper (Manea et al., 2006), and more generally copper dissolution in sulfur ligands solutions (Laglera and van den Berg, 2003).

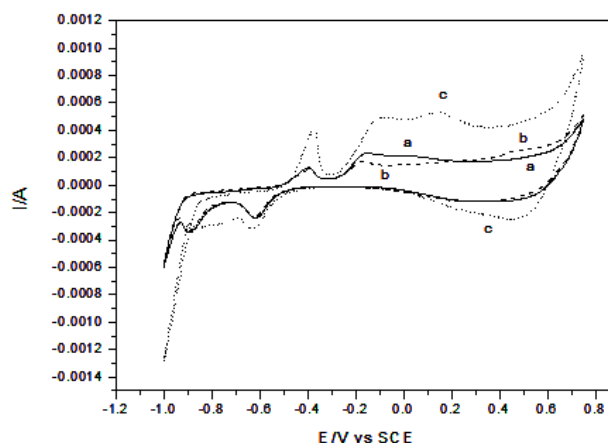


Fig. 1. Voltammetric response (5th scan) of copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte): a – in the absence of organic compound; b- in the presence of 2 mM ASA; c- in the presence of 2 mM TA; starting potential: -0.221 V vs SCE; potential range: $-0.221 \rightarrow +0.75 \rightarrow -1$ V vs SCE; scan rate: 0.05 $\text{V}\cdot\text{s}^{-1}$.

In Fig. 2 the details of the cyclic voltammograms series obtained in the positive

potential range (typical for usual detection of carbohydrates at the copper electrode (Manea et al., 2006)) and the presence of various concentrations of ASA are shown. The values of the current waves around +0.6 V vs SCE increase proportionally with concentrations of ASA. The used detection potential range corresponded to the presumptively mediated oxidation by Cu(II)/Cu (III) system (Manea et al., 2006; Ogovec et al., 1993). The equation of the calibration plots was $I = 1.49 \cdot 10^{-5} + 3.657 \cdot 10^{-5}c$, where I is useful current signal (A) and c is ASA concentration (mM), with a correlation coefficient of 0.988.

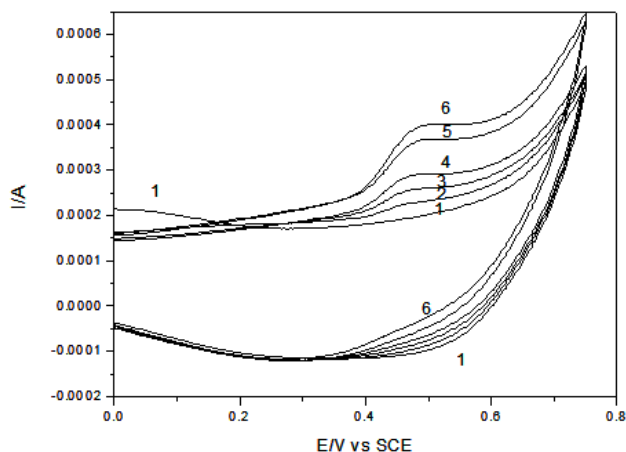


Fig. 2. Detail of voltammetric response (5th scan) of copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte) and in the presence of various concentrations of ASA: 1-0; 2-1 mM; 3-2 mM; 4-3 mM; 5-5mM; 6-6 mM starting potential: -0.221 V vs SCE; potential range: -0.221 $\rightarrow$ +0.75 $\rightarrow$ -1 V vs SCE; scan rate: 0.05 V $\cdot$ s $^{-1}$.

The voltammetric responses of the working electrode in the presence of various concentrations of TA from Fig. 3 corresponded to the characteristic peak of the thiocompounds (Manea et al., 2006) and quantitative aspects were developed in an extended positive potential range. The anodic current increased with concentration of TA in the investigated concentration range. The useful current signal at +0.6 V vs SCE showed a linear dependence current versus concentration, equation being $I = -6.6 \cdot 10^{-6} + 1.5735 \cdot 10^{-4}c$, with a correlation coefficient of 0.996.

An example of the resultant voltammogram obtained in the presence of 3 mM ASA and 3 mM TA in the mixed solution is shown in Fig. 4. In the detection potential range, around +0.6 V vs SCE, the corresponding useful signal from voltammogram c was practically the sum of the individual currents from the individual voltammograms. This overall amperometric signal was the direct and quantitative response of the electrode to the mixed organic load. In addition, the current peak at -0.4 V vs SCE suggested a qualitative distinct evaluation of thiocompound (TA) presence.

3.2. Chronoamperometry data

The dynamic amperometric data from voltammograms were verified complementarily by chronoamperometric data, i.e., quantitative evaluation

of the current-concentration dependence at the fixed potential at a time that corresponds to the conventional steady-state response, e.g., 100 seconds.

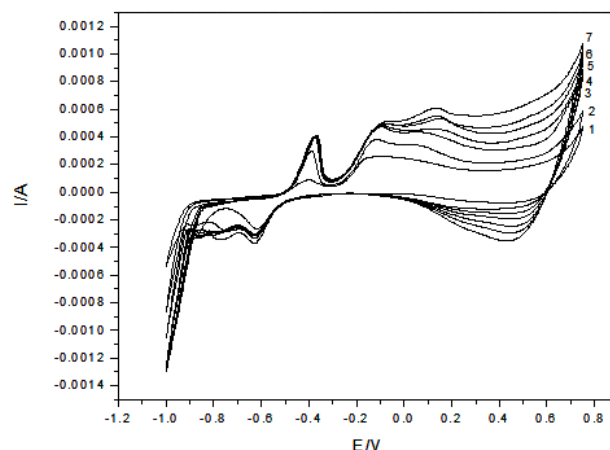


Fig. 3. Voltammetric response (5th scan) of copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte) and various concentrations of TA: 1-0; 2-0.5 mM; 3-1 mM; 4-1.5 mM; 5- 2 mM; 6-2.5 mM; 7-3 mM; starting potential: -0.221 V vs SCE; potential range: -0.221 $\rightarrow$ +0.75 $\rightarrow$ -1 V vs SCE; scan rate: 0.05 V $\cdot$ s $^{-1}$.

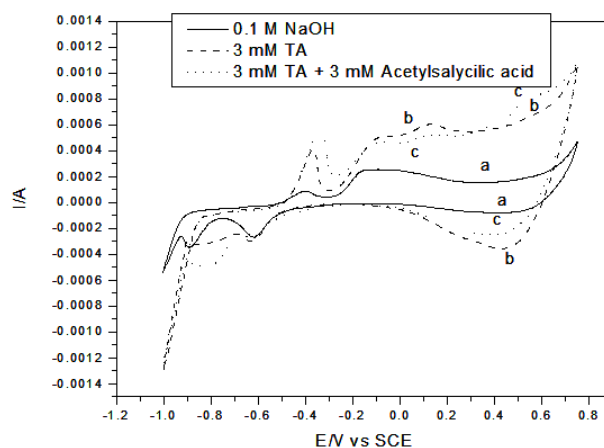


Fig. 4. Cyclic voltammograms of copper oxide-copper electrode in 0.1 M NaOH supporting electrolyte (curve a) and in the presence of: 3 mM TA (curve b) and the mixed solution of 3 mM TA + 3 mM ASA (curve c); starting potential: -0.221 V vs SCE; potential range: -0.221 $\rightarrow$ +0.75 $\rightarrow$ -1 V vs SCE; scan rate: 0.05 V $\cdot$ s $^{-1}$.

Figs. 5 and 6 present the amperometric signal at the +0.6 V vs SCE, due to the presence of TA and ASA. The two variants of the measurements were explored. The first series of the measurements of the current versus time at certain fixed analyte concentrations (Fig. 5), and the second by adding increased analyte concentration and stirred solution (Fig. 6) were performed. The dependences of current versus concentration were linearly and certified the voltammetric data conclusion, and the reproducibility tests were achieved for 5 replicates.

The chronoamperometric response of the working electrode versus overall concentration in the presence of TA and ASA mixed solutions, shown in

Fig. 7 confirmed the overall signals as results of the sum of the individual ones.

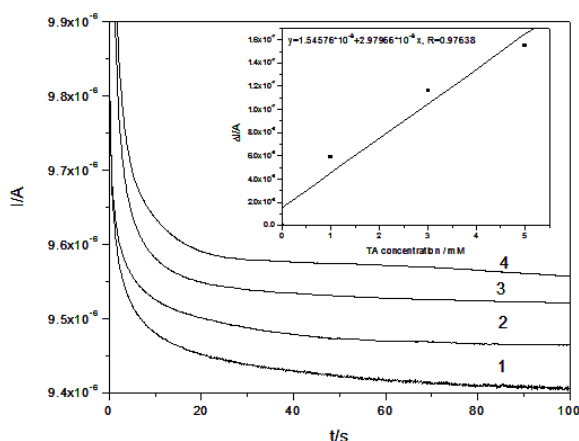


Fig. 5. The steady-state current response of the copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte) and in the presence of various concentrations of TA: 1-0; 2-1 mM; 3-3 mM; 4-5 mM; working potential: +0.6 V vs SCE.

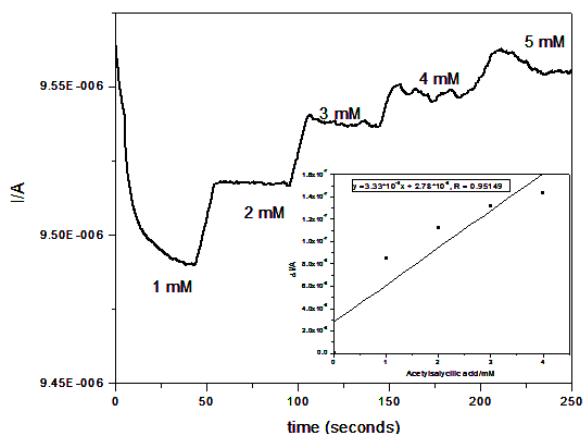


Fig. 6. The steady-state current response of the copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte) for the stepwise additions of various concentrations of ASA: 1-1; 2-2 mM; 3-3 mM; 4-4 mM; 5-5mM; working potential: +0.6 V vs SCE, stirred solution.

Table 1 summarizes the analytical results at 3:1 signal-to-ratio, *i.e.*, calibration characteristics, the detection limits (LOD) and relative standard deviation (RSD) for the tested method by using copper oxide-copper electrode for the electrochemical detection of TA and ASA.

A very good correlation coefficient of 0.94 was established for the linear plots of amperometric signal versus classical COD (A vs mgO₂/L) corresponding to each individual component.

The organic load due to TA and ASA in mixed solutions was checked using both classical COD parameter and amperometric detection. Recovery experiments were performed by adding known amounts of TA and ASA as mixed solution. The classical COD method gave the recovery degree of 65

%, while the amperometric detection gave the recovery degree over 95%.

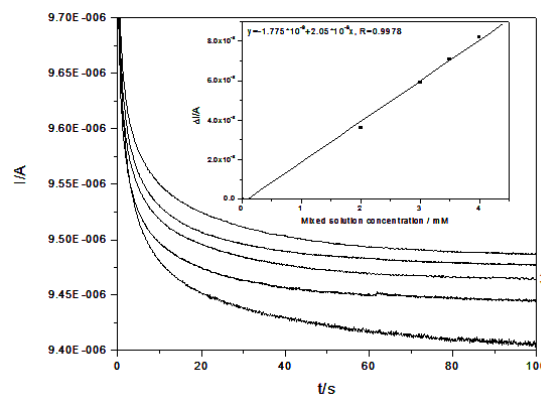


Fig. 7. The steady-state current response of the copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte) and in the presence of various concentrations of TA and ASA mixed solution: 1-0; 2-1 mM TA and 1 mM ASA; 3-1.5 mM TA and 1.5 mM ASA; 4-2 mM TA and 2 mM ASA; working potential: +0.6 V vs SCE, quiescent solution.

Table 1. Some analytical characteristics of ASA and TA for the proposed methods at copper oxide-copper electrode

Target species	Electrochemical method	Electrode sensitivity (A/mM)	LOD (mM)	RSD
ASA	CV	$3.657 \cdot 10^{-5}$	0.4	3.2
TA	CV	$1.57 \cdot 10^{-4}$	0.08	3.6
ASA	CA	$3.33 \cdot 10^{-8}$	0.1	3.0
TA	CA	$2.05 \cdot 10^{-8}$	0.08	3.5
ASA and TA (mixed solution)	CA	$2.98 \cdot 10^{-8}$	0.2	3.7

4. Conclusions

The individual and concomitant amperometric detection of two selected organic compounds regarded as pollutants presented in simulated wastewater was investigated. The use of copper oxide-copper electrode was advantageous as a simple, fast and very accessible way to develop a sensitive and inexpensive method as the alternative to the classical and time-consuming COD parameter.

The optimum potential ranges for quantitative detection of TA and ASA and concomitant qualitative assessment of TA in mixed solution were evaluated from voltammetric measurements and the characteristics of the working electrode.

The linear dependences of the amperometric response versus concentrations were obtained by CV and CA in the individual and mixed systems and finally, verified by the good additivity of the individual amperometric data in overall sum amperometric data.

The recovery degree of the target organics in the mixed solution and the amperometric assessment was over 95%, while for the classical COD assessment only 65%.

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