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Electroreduction of the antifouling agent TCMTB and its electroanalytical determination in tannery wastewaters

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Abstract

The electrochemical reduction of antifouling agent 2-thiocyanomethylthiobenzothiazole (TCMTB) was investigated by cyclic and pulse differential voltammetry. The irreversible electrode reduction of TCMTB proceeded by ECEC reaction mechanism by two electrons transfer with one irreversible wave. Upon the basis of electrochemical evidence, the electrodic reaction mechanism was suggested to formation of mercaptobenzothiazole (MTB) in solution.

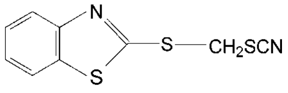
Subsequently, a pulse differential method is described for the formation of TCMTB based on this electroreduction. Having been obtained a detection limit of 1.0×10^{-7} mol L^{-1} and recovery to 98% to concentration of 2.0×10^{-6} mol L^{-1}. Therefore, the proposed method in this study is practical, sensitive and accurate for the analysis of TCMTB in tannery wastewater samples.

Keywords: Wastewater analysis; Fungicide; Pulse differential voltammetry; TCMTB

1. Introduction

The impact of Environment and Health and Safety regulations on the leather industry is becoming wider in scope and more sophisticated. During the past 30 years attention has been directed primarily to such factors as total oxygen demand, and sulphide and chromium levels in tannery waste waters [1–3].

The leather industry has been benefited by the supply of fungicides developed for the protection of other products such as timber, paints and paper [4,5]. Therefore, fungal attack in the leather industry has been prevented by the use of fungicides such as: diuron, TCMTB (2-thiocyanomethylthiobenzothiazole) and chlorothalonil [6]. TCMTB (**1**) which are used in the industry for the preservation of partially processed leather or wood. The biocide formulation is preferentially added to chrome tanning liquor and efficiency of its uptake is controlled by determination of tanning liquors in different times during the process. The major difficulty of such analysis is the instability of TCMTB, which degradates in alkaline solutions, in high temperature, in the presence of sulphide or when exposed to sunlight [7].



(**1**)

Although effective as fungicides, TCMTB and other organic compounds can cause major environmental problems as consequence of their broad toxicity. Research evidence of the damaging effect of triorganotins as TBT (tributyltin) and TCMTB on the environmental has prompted action by many countries to regulate or ban their use as fungicide products.

Several methods for analyzing these compounds in environmental samples can be found in the literature. They are mainly based on liquid-liquid extraction (LLE) or solid-phase extraction (SPE) followed by gas chromatography [8–10] or high performance liquid chromatography coupled to mass spectrometry (HPLC-MS) [11–13]. However, a sensitive methodology for the determination of TCMTB using electrochemical techniques has not yet been described in the

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literature. Besides, the aim of this study is to examine the voltammetric behavior of TCMTB, find out optimum analysis conditions and apply the method for the determination of TCMTB in the tannery wastewater samples.

2. Experimental

2.1. Instrumentation

Voltammetric analysis was performed in an Autolab system PGSTAT20 (EcoChemie, The Netherlands) attached to a Metrohm 663VA stand (Metrohm, Switzerland) and a computer with GPES3 data acquisition software (EcoChimie). The working electrodes, reference and auxiliary were the static mercury drop electrode (HMDE), with a drop area of 0.5 mm × 0.5 mm, Ag/AgCl/3 mol L^{-1} KCl and glassy carbon, respectively.

2.2. Reagents and solutions

Fungicide standard 2-thiocyanomethylthiobenzothiazole (TCMTB) was obtained from ChemService (West Chester, USA) and stock standard solutions (3.0×10^{-3} mol L^{-1}) were prepared in Britton–Robinson (B–R) buffer (pH 2.0). Solutions with pH between 2 and 12 were prepared to 0.04 mol L^{-1} boric acid, 0.04 mol L^{-1} phosphoric acid, 0.04 mol L^{-1} acetic acid and 0.1 mol L^{-1} NaOH. All chemicals were of analytical grade and deionized water was utilized to the preparation of the solutions.

Tannery liquor samples were obtained from tannery industry (Sergipe, Brazil), after biological treatment of the wastewater and natural water was collected to the Fuzil river placed in the same region. The samples were conditioned in 4 °C and light protected.

2.3. Procedures

For electrochemical studies, 5.0 mL buffer containing TCMTB was placed in the cell. Solutions containing 5.0×10^{-5} mol L^{-1} TCMTB was employed for the investigation of the effect of the pH limiting the current and other parameters. The voltammetric experiments were carried out by scanning cathodic against Ag/AgCl reference electrode.

To the application of the method, 20 μL to tannery liquor samples or natural water containing TCMTB were added in 5 mL of the buffer solutions for analysis.

Calibration curves were obtained through successive additions of TCMTB. Three measurements were carried out for each sample and the statistical treatment of the data was carried out according to Miller [14].

3. Results and discussion

In acid medium, TCMTB may be reduced on mercury electrode surface thorough a irreversible process in −1.06 V versus Ag/AgCl (Fig. 1), which shows a nonlinear dependence between current function and scan rate potential in the interval of 20–100 mV s^{-1} (Fig. 2).

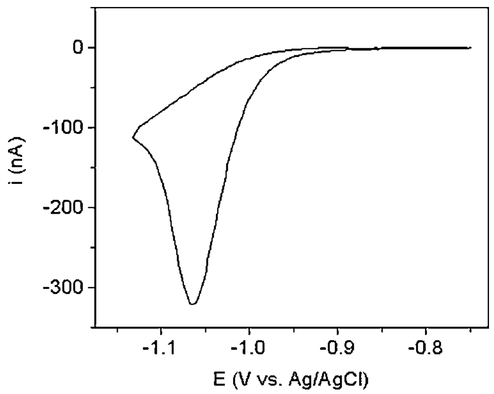


Fig. 1. Cyclic voltammogram of the TCMTB (1.0×10^{-4}) in B–R buffer (pH 3.0), $\nu = 0.1$ V s^{-1}.

This result indicates the presence of adsorptive phenomena as consequence of the high affinity of the TCMTB by the mercury electrode surface.

Coulometric measurements to controlled potential indicated that the peak corresponds to a two-electron reduction process by molecule, which is attributed to the electroactivity of the thiobenzothiazolic group. According to the literature, cleavage is a prevailing and common reactive pathway in the photochemical and metabolic degradation of thiobenzothiazole derivates [15–17]. Although the electrochemical behavior of TCMTB has not been reported, reductive cleavage of thiobenzothiazoles has been previously shown in carbon electrode [18]. Probably the reduction of TCMTB in acid medium happens according to ECEC mechanism as followed by Scheme 1 shown below.

Voltammograms were recorded to examine the effect of the pH on the peak current (i_p) and peak potential (E_p) of 5.0×10^{-5} mol L^{-1} TCMTB employing a differential pulse technique in various pH's (Fig. 3).

The E_p, the potential at peak maximum and i_p, calculated by subtracting the residual current values from the related

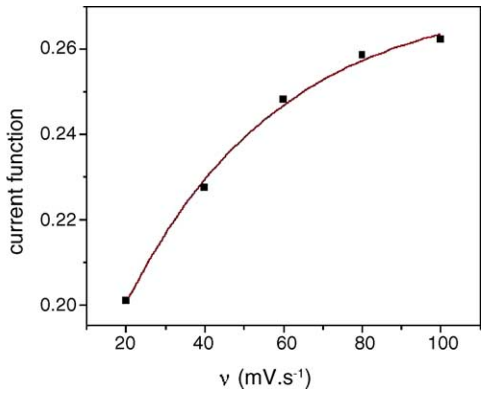


Fig. 2. Behavior of the current function to TCMTB 1.0×10^{-4} mol L^{-1} in B–R buffer (pH 2.0), $\nu = 0.1$ V s^{-1}.

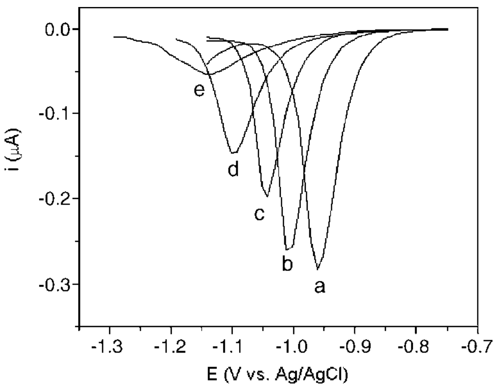


Fig. 3. Pulse differential voltammograms of the TCMTB 5.0×10^{-5} mol L^{-1} in B–R, pHs: (a) 2.0; (b) 3.0; (c) 4.0; (d) 5.0; (e) 8.0. Conditions: $\Delta E = 25$ mV; $\nu = 10$ mV s^{-1}.

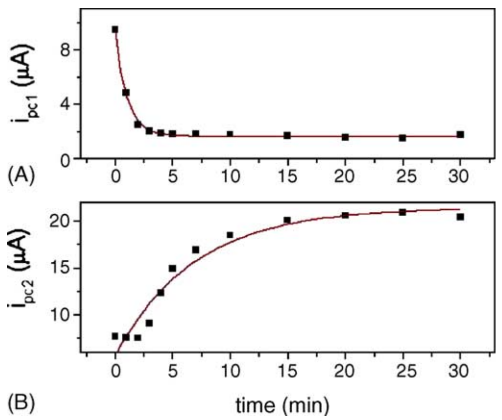


Fig. 5. Decomposition of TCMTB 1.0×10^{-4} mol L^{-1} in buffer B–R/pH 9.0. Conditions: $\Delta E = 25$ mV; $\nu = 10$ mV s^{-1}. (a) TCMTB and (b) MTB.

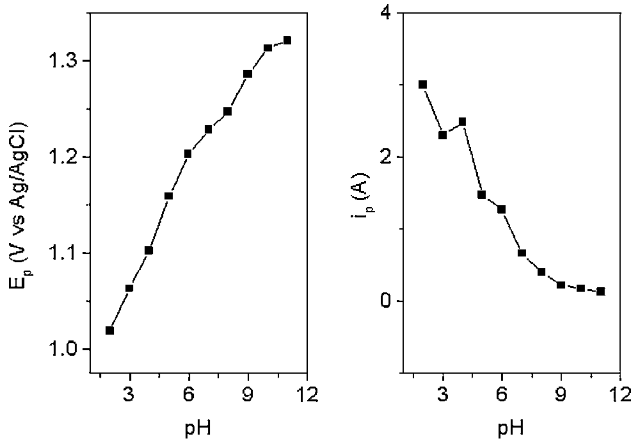
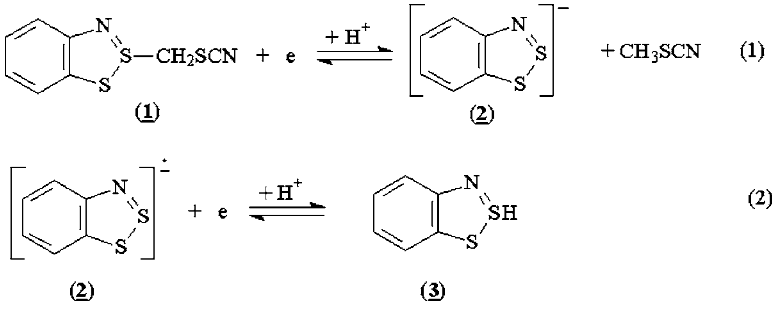


Fig. 4. Effect of the pH on E_{pc} and i_{pc} to TCMTB 5.0×10^{-5} mol L^{-1} in B–R buffer. Conditions: $\Delta Ep = 25$ mV; $\nu = 10$ mV s^{-1}.

peak currents, were taken from the voltammograms and were plotted against pH values. Fig. 4a shows the variation of E_p versus pH being possible to observe that E_p values are pH dependent, where a linear increasing of the potential values occurs to pHs between 2 and 9 (41 mV/pH). This potential shifting can be correlated to the intervention of H^+ in the electrochemical reaction as described in Scheme 1. By parallel, as it is seen from Fig. 4b, i_{pc} values decrease with the pH increase up to the total disappearing of the peak in pH 12, probably due the decomposition of TCMTB in basic medium. In fact, electrochemical measurements showed that the decomposition of TCMTB in basic medium follows a kinetic reaction of first order as can be observed in Fig. 5a and b. The disappearing of the reduction peak that occurs in time function occurs in parallel to the appearing of another peak in a more negative potential (Fig. 6), which can be attributed to the MBT produced during cleavage reaction of the TCMTB in these experimental conditions.

Based on the above results, it is feasible to employ d.p.v. in the quantitative determination of the TCMTB in acid medium. Furthermore, differential pulse voltammograms of 5.0×10^{-5} mol L^{-1} TCMTB were recorded varying pulse heights in the range 2–100 mV. The dependence of peak current versus pulse range indicated to the peak current reached a plateau around 20 mV. Therefore, 25 mV seems to be the most convenient value as pulse height. On the other hand, the best scan rate to the interval between 2 and 20 mV s^{-1} with relation to the resolution of signal is obtained to 10 mV s^{-1}.

The variation of peak current versus concentration of TCMTB in B–R buffer employing optimum voltammetric conditions, which were pulse height of 25 mV and potential speed of 10 mV s^{-1}, was examined. The linear behavior can be described as [$i(A) = 1.6 \times 10^{-10} + 1.5 \times 10^{-4}$ C(mol L^{-1}); $r = 0.9999$, $n = 5$] to the concentration range of 3×10^{-6} to 1.0×10^{-4} mol L^{-1}.



Scheme 1. Mechanism of electrochemical reduction of the TCMTB in acid medium.

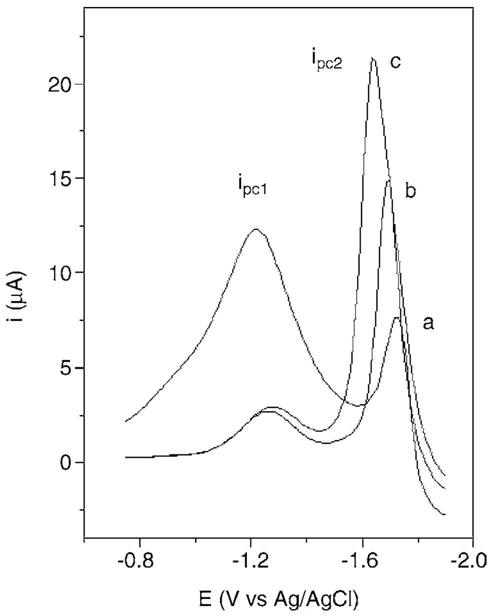


Fig. 6. Decomposition of TCMTB 1.0×10^{-4} mol L^{-1} in buffer B–R/pH 9.0. Conditions: $\Delta E = 25$ mV; $\nu = 10$ mV s^{-1}.

The repeatability of the measurement was adequate, with an R.S.D. of 1.8% on six successive experiments, with a detection limit of 1.0×10^{-7} mol L^{-1}.

The application of the method was achieved by testing the determination using wastewater tannery samples. The samples were processed as described under experimental studies and optimum instrumental conditions were employed for the analysis as illustrated in Fig. 7. The occurrence of TCMTB was not observed, neither in the tannery liquor samples nor in the natural water collected, however, tannery liquor and natural water enriched with TCMTB 5.0×10^{-7} mol L^{-1} presented recovery of 98 and 99%, respectively, which indicates it is a proper method to the analysis of TCMTB in these matrixes.

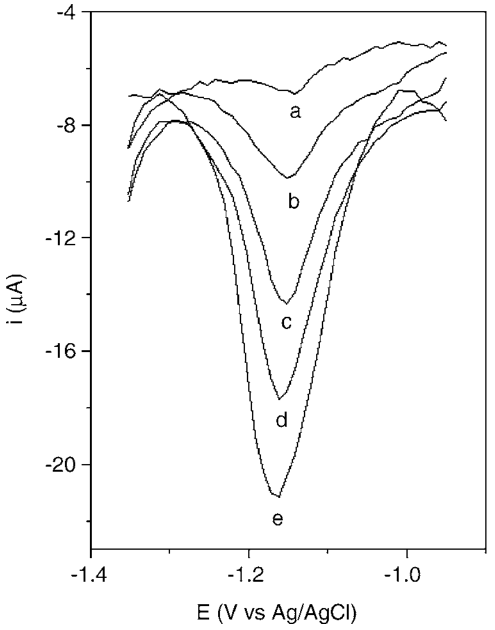


Fig. 7. Voltammograms TCMTB in B–R/pH 3.0: (a) 20 µL sample; (b) 5.0×10^{-6}; (c) 1.0×10^{-5}; (d) 1.5×10^{-5}; (e) 2.0×10^{-5} mol L^{-1}.

4. Conclusion

The electrochemical techniques employed in this study show proper results for analytical application and represent a good alternative for the control of fungicides in natural waters. Sample preparations are easy and the matrix do not interfere in the determination. Consequently, the separation or extraction procedures are not necessary.

Acknowledgement

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