

ELECTROCHEMICAL DETECTION OF TETRACYCLINE AS EMERGENT POLLUTANT IN WATER USING CoAl_2O_4 MODIFIED CARBON NANOFIBER-EPOXY COMPOSITE ELECTRODE

Sorina-Claudia Negrea^{1,2}, Anamaria Baciu³, Raluca Voda³, Florica Manea^{3*}

1- National Institute of Research and Development for Industrial Ecology - (INCD ECOIND)-Timisoara Branch, Bujorilor 115, 300431, Timisoara, Romania

2- "Gheorghe Asachi" Technical University of Iasi, Department of Environmental Engineering and Management, Blvd. Mangeron, 67, 700050, Iasi, Romania

*3- Politehnica University of Timisoara, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Faculty of Industrial Chemistry and Environmental Engineering, V. Parvan 6, 300223, Timisoara, Romania, *e-mail: florica.manea@upt.ro*

Introduction and study objectives

The presence of antibiotics in the environment and especially in water has gained increasing attention. The antibiotics are considered the emergent pollutants in water and the development of their quantitative determination methods has been getting growing attention. Tetracycline antibiotics as one kind of pharmaceuticals and personal care products (PPCPs) are widely distributed environmental pollutants. They are used extensively in veterinary and aquaculture medicine, and excreted to environment with a combination of intact and metabolized pharmaceuticals. The abuse of tetracycline or other antibiotics in aquaculture and farming industry has certain drawbacks, such as antibiotic residues in water and food or provoking allergic symptoms in human. Thus, the identification and detection of these pollutants in environment is important.

Traditional determination methods for determination of tetracycline (TC) depended on large equipment and complicated procedure for sample pretreatment, which were improper for on-site detection or routine analysis. Thus, there is a high demand for a simple, fast, and sensitive method for the determination of tetracycline in water samples. In this context, electrochemical methods with fast and simple operation should be suitable for the determination of tetracycline in water. Also, the electrochemical methods are known to exhibit the great potential for high-performance analytical methods but their performance is in direct relation to the electrode material and the operating techniques. Carbon nanofiber-epoxy composite (CNF) electrode is considered as one class of the appropriate supportive carbon material due to the large surface-to-volume ratio and excellent electrical conductivity for chemically modified electrode characterized by enhanced electrocatalytic and sensing properties.

This paper presents the results obtained for the detection of tetracycline in water using CoAl_2O_4 modified carbon nanofiber-epoxy composite electrode (CNF- CoAl_2O_4) using voltammetric and amperometric techniques.

Methodology

The electrochemical experiments were performed using an Autolab Potentiostat/Galvanostat PGStat 302 (EcoChimie, The Netherlands) controlled with GPES 4.9 software and three-electrode cell

with saturated calomel electrode as reference, platinum electrode as counter-electrode and the carbon nanofiber-epoxy composite electrode (CNF) modified with cobalt aluminate CoAl_2O_4 as working electrode. The electrode CNF was modified by simple immersion within an aqueous suspension (10 mg mL^{-1}) of cobalt aluminate CoAl_2O_4 .

Results and conclusions

The electrochemical techniques applied for electrochemical characterization and analytical applications were cyclic voltammetry, square-wave voltammetry and chronoamperometry. Square-wave voltammetry operated under optimized working conditions, *i.e.*, step potential of 10 mV, modulation amplitude of 200 mV and frequency of 20 Hz, allowed reaching the best sensitivity of $13.04 \mu\text{A}\mu\text{M}^{-1}$ and the lowest limit of detection of $0.023 \mu\text{M}$ for TC determination in water.

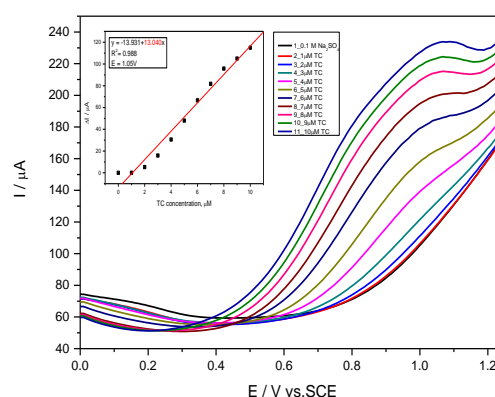
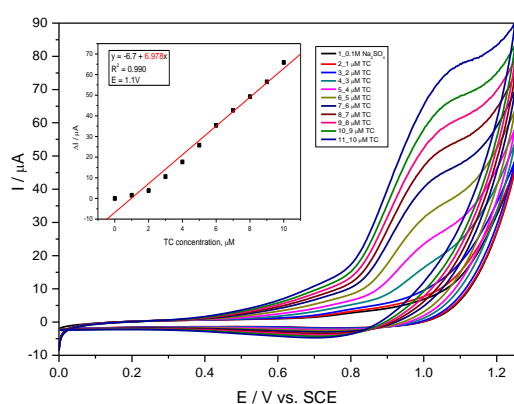


Fig.1. Cyclic voltammograms recorded on CNF- CoAl_2O_4 electrode in 0.1 M Na_2SO_4 supporting electrolyte and various TC concentrations; Inset: Calibration curve of current vs TC concentrations;

Fig.2. Square-wave voltammograms recorded on CNF- CoAl_2O_4 electrode in 0.1 M Na_2SO_4 supporting electrolyte and various TC concentrations; Inset: Calibration curve of current vs TC concentrations;

Based on the results of this study, it can be concluded that CoAl_2O_4 modified carbon nanofiber-epoxy composite electrode is appropriate for tetracycline detection in water and the future work will consider the other antibiotics in real water.

Acknowledgement: This work was supported partially by a grant of the Romanian Ministry of Research and Innovation, project number PN-III-P1-1.2-PCCDI-2017-0245/26 PCCDI/2018 (SUSTENVPRO), within PNCDI III and partially by research grant GNaC2018 - ARUT, no. 1350/01.02.2019, financed by Politehnica University of Timisoara