Investigation of Electrochemical Detection of Nitrite and Nitrate in Water for Environmental Application

Malak Talbi[a,b*], Ammar Al-Hamry[a], Tianqi Lu[a], Mounir Ben Ali[b,c] and Olfa Kanoun[a*]

[a]Professorship of Measurement and Sensor Technology, Technische Universität Chemnitz, Reichenhainer Str.70, 09126 Chemnitz, Germany*malak.talbi@etit.tu-chemnitz.de, olfa.kanoun@etit.tu-chemnitz.de*, tianqi.lu@etit.tu-chemnitz.de, ammar.al-hamry@s2011.tu-chemnitz.de
[b]NANOMISENE Lab, LR16CRMN01, Centre for Research on Microelectronics and Nanotechnology of Sousse, University of Sousse, Sousse 4034, Tunisia, malak.talbi@etit.tu-chemnitz.de, mounirbenaliissat@gmail.com
[c]Electronic Department, University of Sousse, Higher Institute of Applied Science and Technology of Sousse, 4003 Sousse, Tunisia, mounirbenaliissat@gmail.com

Abstract:
This paper is about electrochemical investigations of nitrite (NO_2^-) and nitrate (NO_3^-) detection in water. Herein, a study based on functionalization of carbon screen-printed electrodes (CSPE) with chitosan and tetrasulfonated copper (II) phthalocyanine nanocomposite (Chit/Ts-CuPc). Cyclic voltammetry (CV) surveys were carried out with ferri/ferrocyanide probe and analytes for preliminary investigations to confirm the efficacity of the electrode's functionalization. Differential pulse voltammetry (DPV) measurements then were performed for more precise and sensitive detection with different analytes concentrations. Further studies regarding pH optimization, electrodes kinetics and calibration curve will be performed to calculate the sensor's figures of merits. As well as a real sample test is to be done to prove that the developed sensors are very promising for effective nitrite and nitrate detection.

Keywords: Nitrate; Nitrite; Nanocomposites; Electrochemical detection

1. INTRODUCTION

The nitrogen cycle, involving the atmosphere, land and water ecosystems, and their related flora and fauna, has a major impact on the food chain and, therefore, on the environmental quality. Nitrogen is integrated into nitrogenous compounds by several routes, such as by microorganisms, plants and industrial agro-aqua cultural resources [1]. In these pathways, nitrites (NO_2^-) and nitrates (NO_3^-) are involved, which are natural elements of crops and vegetables [2]. Nitrites and nitrates are molecules of great concern in the healthcare and environmental protection areas because of their heavy application in fertilizing agents and well-known additives in food products recorded as official preservatives (European Commission, 2011). In the food industry, they have been used as additives for a quite long time. They mainly serve to control the propagation of microorganisms causing food intoxication and to prevent the development of extremely dangerous bacteria such as Clostridium botulinum that produce botulin toxin that causes paralysis and neuronal problems [3][4]. As well, nitrite is found to be used in meat because it reacts with meat myoglobin keeping the red color for treated meat. However, the uncontrolled use of either nitrite or nitrate can put public health and the environment in risk. NO_2^- may cause an irreversible reaction with hemoglobin, resulting in the production of methemoglobin, which limits the blood's ability to carry oxygen. Additionally, in the human gastric system nitrites interact with amines and amides to produce N-nitrosamine complexes, which are carcinogenic [5][6]. In addition, levels of NO_3^- need to be monitored, particularly in meat products, mainly because in the favorable environment of the gastrointestinal tract, NO_3^- can be reduced to NO_2^-. Monitoring these potentially harmful environmental compounds, will play a significant role in enhancing the quality of human life through the surveillance of potentially hazardous substances and subsequent removal of harmful contaminants from the aquatic environment[7-9]. Environmental Protection Agency's (EPA's) and the world health organization guidelines (WHO) recommended limits for nitrates and nitrites intakes in drinking water and food. EPA has assigned an enforceable guideline called the maximum contaminant level (MCL) in water for nitrate at 10 ppm (10 mg/L) and nitrite at 1 ppm (1 mg/L) [10][11]. The permissible limit of nitrite concentration in the drinking water is 3 mg/L, according to WHO [12]. As a result, the development of analytical sensors that can provide appropriate and sensitive information has gained considerable focus in recent years to investigate and solve water quality concerns [13]. Some studies investigated the simultaneous determination of nitrate and nitrite, such as in [14], a GC electrode based on Cu metal nanoparticles decorated on MWCNTRGO nanocomposite. Also, a bienzymatic biosensor system using copper, zinc superoxide dismutase
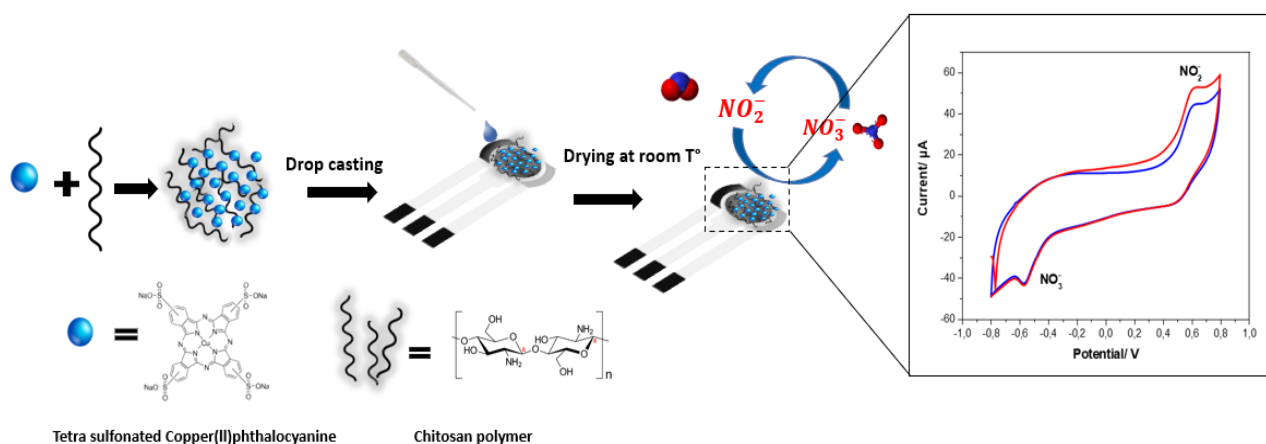
Figure 1: Overview of the modification of CSPE with Chit/ Ts-Cu(II)Pc nanocomposite for nitrite and nitrate electrochemical investigations

(SOD1) and nitrate reductase (NaR) coimmobilized electrode[15]. Another procedure proposed[16], for nitrite and nitrate quantification in different samples based on nano-composite carbon paste electrode fabricated from L-SCMNPs.

Detection of these ions have been reported by use of several techniques[17] such as spectrophotometry [18][19], chromatography [20][21][22], chemiluminescence [23][24], colorimetry [25] and electrochemistry [26][14][27]. Electrochemical approaches proved to be very much favoured among others for providing a sensitive, rapid, and cost-effective detection method, and especially, it enables the on-site implementation of the developed analytical approach [9]. The use of the electrode modified with nanocomposite materials further increases the sensitivity and selectivity and drives the development of analytical methods adapted to the application in real samples [13][28][29][30]. The electron transfer between electrodes surfaces and analytes is favorable and considerably enhanced with selective functionalization of the electrodes based on the chemical structure of the contaminant. Various nanomaterials have been applied for the detection of NO_2^-, NO_3^- such asmetallophthalocyanines (MPCs), carbon nanomaterials, metallic nanoparticles, and polymers is growing for application in electrochemical sensors[31][32][33][34].

In this contribution, an electrochemical sensor for nitrite and nitrate measurement is developed using functionalized carbon screen-printed electrodes with Chit-TsCuPc nanocomposite.

2. EXPERIMENTAL SECTION

2.1. Devices, materials and chemicals

Standard nitrite, nitrate solutions were prepared with sodium nitrite and sodium nitrate. Sodium phosphate (dibasic heptahydrate and monobasic monohydrate) was used to prepare phosphate buffer solutions (PBS). Cu(II)Pc salt and MWCNTs were used for phosphate investigations. Chitosan and Ts-Cu(II)Pc salts were used for nitrite and nitrate investigations. All chemicals needed were purchased from Sigma-Aldrich and did not require additional purification. Screen-printed electrodes with carbon working electrode, Ag/AgCl reference, and carbon counter electrodes (ItalSens IS-C) are purchased from PalmSens BV, Houten, Netherlands. All electrochemical measurements were carried out with the PalmSens 4 potentiostat, which is also acquired from PalmSens BV.

2.2. Sensor's preparation

Chit/Ts-Cu(II)Pc nanocomposite was synthesized based on a procedure published in [35]. First, Ts-CuPc solution with a concentration of 5 mg/L was prepared by suspending 50 mg of TsCuPc powder in 50 ml of distilled water. 1 g of chitosan was suspended in 100 ml of distilled water, followed by the addition of 1 g of glacial acetic acid to improve the dispersion. Then the solution was stirred until a stable dispersion of chitosan is obtained. After, the mixture is concentrated until obtaining 10 mL in a rotary evaporator. The obtained nanocomposite is stored in dark for further use. For nitrite and nitrate investigations, the concentrated chit-TsCuPc nanocomposite was dispersed in 5 mL of ethanol and ultrasonicated for 1 h. Then 3 µL of the colloidal suspension of Chit-TsCuPc was drop casted onto the surface of CSPE and dried at room temperature. The surface electrode modification process and electrochemical analysis of nitrite and nitrate are shown in fig.1a.

3. RESULTS AND DISCUSSION

To investigate the performance of the prepared modified electrode with Chit-TsCuPc, a redox probe

test with in Ferri/ferrocyanide was first tested, then the electrochemical behaviour of nitrate and nitrite ions were studied with CV and DPV in 0.1 M of PBS buffer/pH 7 [35] (pH 7 is used for preliminary investigations and a further pH ranges to be studied to select best response) with 0.001 M of NO_2^- an NO_3^-. The cyclic voltammograms in fig. 2 show two well-defined anodic and cathodic peaks of analytes only with the modified electrode. The oEnvironmentalxidation peak of NO_2^- is observed at 0.5 V and the reduction peak of NO_3^- is observed at -0.58 V (with a scan rate of 0.05 V/s). However, the unmodified electrode showed no reactions towards the simultaneous presence of nitrite and nitrate.
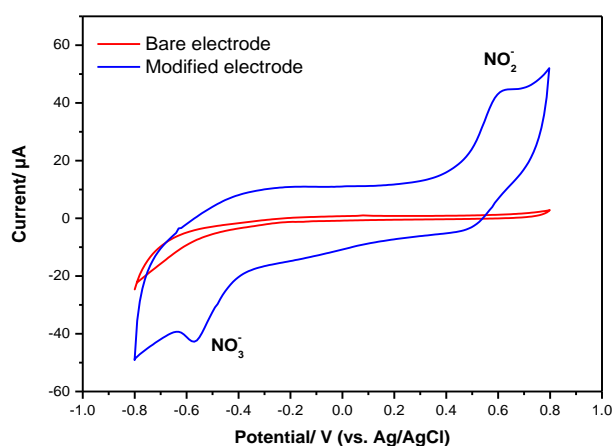

Figure 2: Cyclic voltammograms of bare and functionalized CSPE in 0.001 M of nitrite and nitrate in 0.01 M of PBS buffer with 0.05 V/s scan rate

This can be due to the catalytic effect and strong enhancement in the electron transfer rate of analytes on the Chit-TsCuPc electrode. According to the literature, the chemical reaction between nitrite and nitrate mechanism could occur by two successive, one-electron oxidation steps given by the following elementary reversible reaction equation (1) [36]:

$$NO_2^- + H_2O \leftrightarrow NO_3^- + 2H^+ + 2e^- \qquad (1)$$
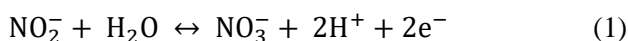
The choice to cover both nitrate and nitrite as simultaneous detection has gained increasing interest and the choice was done on the basis of their linked chemistries and one of them is rarely present without the other.

It can be seen as illustrated in fig. 3 where after modification with Chit-TsCuPc/ CSPE the peak currents in DPV increased markedly. Oxygen has no interference with both nitrates and nitrites, the high current capacitive behaviour is due to the adsorption of nitrates on surface before reduction.
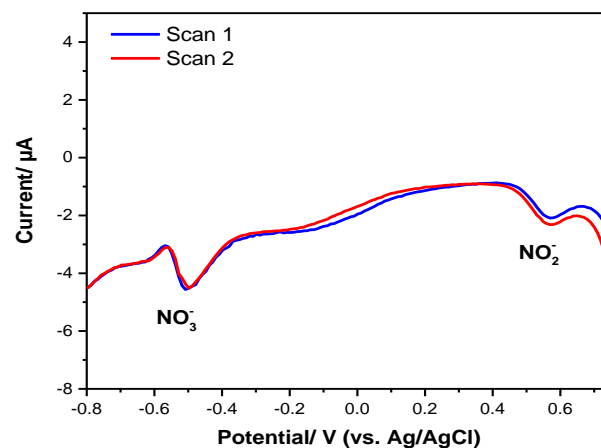Further electrochemical studies will be carried out based on DPV measurements.

Figure 3: Differential pulse voltammograms of functionalized SPE in 0.001 M of nitrite and nitrate with 0.05 V/s scan rate

4.   SUMMARY

This paper discusses the investigations performed to evaluate the feasibility for the development of electrochemical sensors for the detection of NO_2^- and NO_3^- simultaneously with Chit-TsCuPc. These sensor showed the ability of detection of ions in water, and further experiments will be tested in real samples such as food and soil samples. Improvements of the study will use further electrochemical techniques and calculate sensor parameters such sensitivity, limit of detection and selectivity. Proof of concept and feasibility of the developed nanomaterials are achieved.

5.   Acknowledgment

6.   References

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