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Simultaneous voltammetric detection of ammonium and nitrite from groundwater at silver-electrodecorated carbon nanotube electrode

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ABSTRACT

Ammonium and nitrite are listed by Water Framework Directive as core parameters that should be monitored for the groundwater as drinking water source. This work describes the sensitive protocols for the simultaneous detection of ammonium and nitrite in water at a new silver-electrodecorated carbon nanotubes-epoxy composite electrode (Ag-CNT) using advanced voltammetric technique. A carbon nanotubes-epoxy composite electrode obtained by two-roll mill procedure was decorated electrochemically with silver nanoparticles. This new electrode displays excellent electrocatalytic activity towards the direct oxidation of ammonium and nitrite at well separated less potential values (+0.15 V/SCE for ammonium and +0.7 V/SCE for nitrite). Very good detection sensitivities (0.613 mA mM⁻¹ for ammonium and 0.980 mA mM⁻¹ for nitrite) and the lowest limits of detection (1 μM for ammonium and 0.7 μM for nitrite) were achieved by differential-pulsed voltammetry (DPV) under optimum operating conditions of 0.05 V step potential, 0.2 V modulation amplitude and the scan rate of 0.05 V s⁻¹. This detection protocol was successfully applied to the simultaneous determination of ammonium and nitrite in groundwater samples, and the results were found to be consistent with the values obtained by the standardized spectrophotometry methods.

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1. Introduction

Nitrogen compounds are ubiquitous in nature. They exist naturally as nitrogen cycle in the environment in several forms as gaseous nitrogen, ammonia nitrogen, nitrates, nitrites and organic nitrogen. For water there are the regulations for the maximum allowance concentrations for the nitrogen-based compounds in the direct relation with the water type, e.g., groundwater, surface and wastewater.

Groundwater and surface water are very important sources for drinking water and the maximum allowance concentrations are set by Drinking Water Directive (ECC) as 0.5 mgL⁻¹ for each ammonium and nitrite compound. Also, in the framework of the protection and conservation of all water bodies to achieve "good" quality status that is known as the main objective of the Water Framework Directive, the ammonium and nitrite are listed as core parameters that should be monitored for the groundwater as drinking water source

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(2000/60/EC, WFD), Nitrites presence in water occurs by both natural and anthropogenic processes. The natural processes consist of the oxidation of ammonia or reduction of nitrate by microorganisms in plants, soil and water, being intermediate species in the nitrogen cycle. From the point of the anthropogenic process, nitrite presence in water can be a result of excessive use of fertilizer, as a result of defective management practice in farming activity, inappropriate treatment of the wastewater related to the biological step based on nitrification-denitrification processes, or discharges from industrial and mining processes (Baciu et al., 2015; Yilong et al., 2015). Also, it is well-known the negative effect of the nitrite on the human health to produce diseases like stomach cancer or methemoglobinemia (Santos et al., 2009; Sahraoui et al., 2013).

Ammonium is formed naturally in groundwater as a result of the reaction of biochemical decomposition of organic nitrogen compounds and reduction of nitrites and nitrates (Hussaian et al., 2015). It is also, commonly found in groundwater due to anthropogenic activities, mainly due to leaching from fertilizers, municipal waste disposal, leaking from animal farm waste. Ammonium concentrations exceeding the imposed limit indicates a sanitary water pollution (Bohlke et al., 2006), and contributes to the eutrophication process of surface water.

There are a lots of methods for the determination of individual nitrite and ammonium, based on spectrometry (Garcia-Robledo et al., 2014; Krom, 1980), ion-chromatography (Michalski and Kurzyca, 2006), flow-injection analysis (Kazemzadeh and Ensafi, 2001; Nobrega et al., 1995). Also, HPLC have been developed that are faster, more accurate and more sensitive than spectrophotometric methods. However, the most methods are often laborious to perform and require chemical reagents (Chou et al., 2003; Mesequer-Lloret et al., 2005).

Several electrochemical methods have been reported for the quantitative assessment of individual ammonium and nitrite, most of them are based on the potentiometric principles using ion-selective sensors (Molins-Legua et al., 2006; Yilong et al., 2015), and other are based on voltammetric/amperometric techniques (Najafi and Darabi, 2014; Badaea et al., 2009). The electrochemical methods have been developed as reliable and inexpensive sensing methods with low limit of detection and high sensitivity that are in direct relation with the electrode material and the electrochemical techniques (Baciu et al., 2015; Manea et al., 2010). On the strength of this matter, many efforts have been directed to the enhancement of the performance of the voltammetric techniques. Differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) are very operative for electroanalysis application due to their high sensitivity based mainly on background current minimization (Molina et al., 2011). There are reported papers related to the applications of voltammetric techniques to detect and monitor the nitrite and ammonium at a bare solid electrode, e.g., copper electrode (Davis et al., 2000; Dutt and Davis, 2002), palladium electrode (Milhano and Pletcher, 2008), platinum electrode (Wu et al., 2004), gold electrode (Silva and Mazo, 1998), glassy carbon electrode (Kozub et al., 2010). However, the determination of nitrite and ammonium on a bare solid electrode is difficult due to slow electron transfer rate and surface passivation effect (Yilong et al., 2015). To overcome these disadvantages, the modifications of the electrode surface with a suitable catalyst have been proposed. Several types of carbon have

been used as a substrate for various catalysts to detect nitrite and ammonium, e.g., copper-graphite electrode (Kaminskaya et al., 2004), gold nanoparticle composite coated glassy carbon electrode (Huang et al., 2008), carbon black modified electrode (Malha et al., 2013), potassium doped graphene electrode (Li et al., 2012), iridium modified carbon fibre (De et al., 2000), lead oxide graphite composite electrode (Sljukic et al., 2007).

In addition, nanoparticles-type catalysts exhibit specific peculiarities to enhance the electroanalytical performance related to the sensitivity and the lowest limit of detection by the larger electroactive surface area and higher electrocatalytic effect towards the reduction or oxidation process responsible for the electroanalytical response (Inngam et al., 2012; Wang et al., 2012; Qu et al., 2015).

To our knowledge, there are no reports about the simultaneous electrochemical detection of ammonium and nitrite in aqueous matrices. The aim of our study was to develop electroanalytical strategies based on certain advanced voltammetric techniques for the simultaneous and sensitive detection of ammonium and nitrite anions in aqueous solution using a specific silver-electrodecorated carbon nanotubes-epoxy composite electrode (Ag-CNT). Direct oxidation of both ammonium and nitrite on this specific electrode and as consequence, their determination were investigated by cyclic voltammetry (CV). Square-wave (SWV) voltammetry and differential-pulsed voltammetry (DPV) techniques-based procedures were tested, developed and optimized for selective and simultaneous detection of ammonium and nitrite.

2. Experimental

2.1. Materials

The epoxy resin used in the study was Araldite®LY5052/Aradur®5052 purchased from Huntsman Advanced Materials, Switzerland. Carbon nanotubes synthesized by catalytic carbon vapor deposition were produced by Nanocyl™, Belgium. Their main characteristics consisted of 90% carbon purity, 90% CNT content, average diameter of 9.5 nm, average length of 1.5 μm, and surface area of 250–300 m²/g.

2.2. Preparation of CNT-based composite electrodes

The dispersion of CNT in tetrahydrofuran were achieved by ultrasonication about 10 min prior to mixing with the polymer resin. After the sonication process, the solutions of CNT-THF were sonicated again with epoxy resin to obtain a more homogeneous mixture. An effective two roll mill method was used to prepare the electrodes in order to achieve high levels of dispersion and distribution. The details of the preparation methods have been already published elsewhere (Manea et al., 2012). The ratio between the components was chosen to reach 20%, wt. CNT and respective, 20%, wt. epoxy resin. The mixture was then poured into PVC tubes and cured in a vacuum oven at 80 °C for 24 h, followed by cooling down at room temperature, and the composite electrode with disc surface area of 19.63 mm² was obtained. The electrical contacts of the electrodes were assured using copper wire. Then, the surface of the obtained electrode was decorated with silver by electrodeposition at a constant potential of –0.4 V vs. SCE for 10 s in the presence of 0.1 M AgNO₃ solution.

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