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Screen-printed electrode modified with carbon black nanoparticles for phosphate detection by measuring the electroactive phosphomolybdate complex

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ABSTRACT

We report a sensor for phosphate detection based on screen-printed electrodes modified with carbon black nanoparticles. The phosphate was measured in amperometric mode via electrochemical reduction of molybdophosphate complex. Carbon black nanoparticles demonstrated the ability to quantify the molybdophosphate complex at a low applied potential. Some analytical parameters such as the working solution (sulfuric acid 0.1 M), applied potential (0.125 V vs Ag/AgCl), and molybdate concentration (1 mM) were optimized. Using these conditions, a linear range of 0.5–100 μM was observed with a detection limit of 0.1 μM, calculated as three times the standard deviation of the blank divided by the slope of calibration curve. The system was challenged in drinking, river, aquarium, and waste water samples yielding satisfactory recovery values in accordance with a spectrophotometric reference method which demonstrated the suitability of the screen-printed electrode modified with carbon black nanoparticles coupled with the use of molybdate to detect phosphate in water samples.

1. Introduction

Phosphate is an important compound for all living organisms because it is necessary for deoxyribonucleic acid (DNA) and adenosine triphosphate (ATP) synthesis. Furthermore, it is an essential nutrient for plants, but at high concentrations it creates a condition called eutrophication with a rapid growth of the plant population (algal blooms) in aquatic environments [1–3]. The importance to reduce the phosphate release into the environment was highlighted by 2000/60/EC directive [4], and waste water treatment facilities are obliged to meet phosphate discharges. In order to control the phosphate amount in waters, reliable analytical methods for phosphate detection are required. The reference method is based on ammonium molybdate and orthophosphate reaction in acid medium in presence of a catalyst to form a phosphomolibdic heteropolyacid (HPA); thus the complex is reduced by ascorbic acid to obtain a blue colored molybdenum complex that is measured spectrophotometrically [5]. Despite the good sensitivity and reproducibility of this method, the colorimetric analysis suffers from interferences arising from silicates and arsenates; moreover, it is time consuming, requires fresh reagents due to the poor stability of some of them such as ascorbic acid, and it cannot be applied on colored samples.

The detection of phosphorus species is also carried out using ion chromatography, which is highly sensitive (down to ppb levels) and selective technique, but requires skilled personnel, laboratory setup, and expensive instrumentation [6].

Currently, many research lines are focused on the development of analytical methods able to overcome the drawbacks discussed above. In this context, electrochemical methods are a good alternative for their characteristics such as cost-effectiveness, easiness of miniaturization, high sensitivity and the capability to analyze colored samples [7,8].

The strategies of electrochemical phosphate detection include the use of ion selective electrodes [9,10], electrochemical biosensors based on mono- or multi-enzymatic reactions [11,12] and amperometric sensors [13–15]. In the last case, molybdate is often employed as reagent in order to obtain molybdophosphate complex which is electrochemically reduced. The approach is similar to the reference spectrophotometric method reported before, where instead of the chemical reducing agent, a reduction potential was applied with the advantage to avoid the complications due to the limited stability of the chemical reducing compounds [16,17]. The electrochemical detection of molybdophosphate complex was reported in literature by using molybdate in solution and carbon paste electrodes [18], gold microdisk electrodes [19,20], and glassy carbon electrodes [21]

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reaching a detection limit at μM level. The ammonium heptamolybdate was also immobilized into a glassy carbon electrode surface as precursor [14], or in addition the molybdate ions were produced in situ by anodic oxidation of molybdenum [22].

In order to develop a miniaturized and cost-effective sensor, screen-printed electrodes (SPEs) are a valuable choice. However, SPEs often require electrochemical [23] or plasma [24] treatment to improve their electrochemical performances as well as their modification with nanomaterials such as gold nanoparticles [25,26], carbon nanotubes [27,28], and graphene [29,30]. Among the various nanomaterials, carbon black has demonstrated to possess valuable electrocatalytic properties for analyte detection in solution, as reported by our research group in 2010 [31], and from this point onwards, several investigations carried out by other groups and us have confirmed the relevant electrochemical properties of carbon black nanoparticles (CBNPs) [32–38]. In detail, the CBNPs modified sensor was tested with ferricyanide as electrochemical probe, observing a decrease of peak to peak separation, and when this sensor was tested with several analytes such as NADH, H_2O_2, and cysteine, a reduction of overpotential and an increase of sensitivity were observed. The reason of this enhancement can be ascribed to the high number of its defect sites. In fact, CB N220 is characterized by I_D/I_G ratio equal to 0.96 (I_D/I_G ratio is a measure of the number of disorder and defect sites in the graphitic carbon). Furthermore, low peak to peak separation can be also explained by the effect of diffusion within a porous layer of nanomaterial as reported by Compton's group in the case of electrode modified with carbon nanotubes [39]. The advantage of using CBNPs is not related to the CB N220, but other carbon blacks have also demonstrated good electrochemical properties, such as CB M1100 for adsorptive stripping voltammetry analysis of nicotine, as reported by Compton's group [35], or CB VXC72R, as reported by Vicentini et al. [38].

In this work the electrochemical properties of CBNPs were exploited in the phosphate detection by means of the electrochemical reduction of molybdophosphate complex. The applicability of SPE modified with CBNPs (CBNPs-SPE) was also demonstrated in several water samples.

2. Experimental

2.1. Apparatus and reagents

Cyclic voltammetry (CV) and amperometric measurements were performed using a portable PalmSens Instrument (PalmSens, The Netherlands) in connection with a personal computer.

Nitric acid 70%, sulfuric acid 95–98%, hydrochloric acid 37%, ammonium heptamolybdate tetrahydrate, potassium chloride, potassium dihydrogen phosphate as reagent grade and sodium metasilicate were purchased from Sigma-Aldrich.

2.2. SPE preparation

Screen-printed electrodes (SPEs) were home-produced with a 245 DEK (Weymouth, UK) screen-printing machine [33]. Graphite based ink (Electrodag 421) from Acheson (Milan, Italy) was used for printing the working and counter electrodes. The pseudoreference electrode used is constituted of silver ink (Electrodag 477 SS), and in order to obtain a stable applied potential, to the working solution of sulfuric acid, KCl (0.1 M) was added.

The substrate was a flexible polyester film (Autostat HT5) obtained from Autotype Italia (Milan, Italy). It was produced in foils containing 48 sensors. The diameter of the working electrode was 0.3 cm, resulting in a geometric area of 0.07 cm^2.

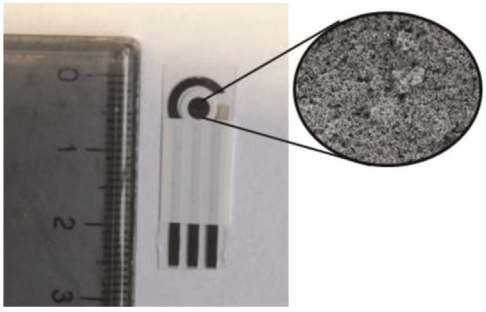

Fig. 1. Photo of an SPE modified with CBNPs. Inset: SEM image of the working electrode modified with CBNPs.

2.3. CBNPs dispersion

The dispersion of CBNPs was prepared adding 20 mg of CB powder to 20 mL of solvent (a mixture dimethylformamide (DMF: water (1:1))) sonicated for 60 min at 59 kHz [33].

2.4. Preparation of CBNPs-SPE

The SPE was modified with CBNPs via drop casting pipetting a small volume (6 μL) onto the working electrode surface of the SPE in three steps of 2 μL each [31–34]. After, the solvent was allowed to volatilize, forming a carbon black "film" on the electrode surface (CBNPs-SPE, Fig. 1). The CBNPs-SPEs were maintained in dry condition before the use, and these sensors are stable for at least 100 days, as demonstrated in our previous work [33].

2.5. Electrochemical phosphate measurement

Phosphate measurements were carried out in amperometric batch analysis with CBNPs-SPEs in 10 mL of stirred H_2SO_4 0.1 M+KCl 0.1 M with an applied potential of 0.125 V vs Ag/AgCl. When a stable baseline current was reached, the molybdate was added and the current registered; after that, the analyte was added and the response was recorded. The current was calculated as the difference between the response of molybdate in presence and in absence of phosphate.

2.6. Spectrophometric phosphate measurement

The spectrophotometric measurements were performed following the procedure reported in literature [5]. The stock solution of phosphate was added to double distilled water in order to obtain 5, 10, 40 μM as final concentrations. The mix reagent (800 μL) containing 5 ml of heptamolybdate (24.3 mM), 2.5 ml of potassium antimonyl tartrate (2 mM), and 12.5 ml sulfuric acid (2.8 M) was added to each standard solutions and then mixed for 15 min. After that, the reduction of phosphomolybdic complex was obtained adding the ascorbic acid solution (200 μL of 0.31 M aqueous solution) as reducing agent. The absorbance was measured after 10 min at 831 nm.

2.7. Phosphate detection in water samples

Tap water samples were collected at Rome Tor Vergata University, river water samples from Liri river (RM, Italy), aquarium water samples from the aquarium of one of the authors, and the sample of waste water was supplied by Tover Italia, Rome (paint industry).

These samples were analyzed by spectrophotometric and amperometric methods, as described in details below, and in the