Journal of Electroanalytical Chemistry 813 (2018) 58–66

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Low symmetric metallophthalocyanine modified electrode via click chemistry for simultaneous detection of heavy metals

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ARTICLE INFO

Keywords:
Cobalt phthalocyanine
Click reaction
Heavy metals
Electrochemical sensor

ABSTRACT

Beside different methods and materials used to develop electrochemical sensors, the modification of the electrode using click reaction based on metallophthalocyanine (MPc) compounds are shown to improve the stability and sensitivity of the sensor. This work reported the development of electrochemical sensor for mercury (II), Lead (II), copper (II) and cadmium (II) ions detection based on the synthesized novel low symmetry alkyne terminated cobalt Phthalocyanine (CoPc) derivative. Differential pulse stripping voltammetry (DPSV) technique was employed for the first time in simultaneous determination of trace levels of the above metal ions using modified glassy carbon electrode (GCE) via click chemistry. Under the optimum experimental conditions, the anodic peak current is proportional to the concentrations of metal ions over a wide range of 0 to 0.1 mM with nanolevel detection limit of 81.94, 327.71, 55.87 and 347.06 nM and the sensitivity of 866.23 ± 5.48, 215.82 ± 2.16, 1979.48 ± 11.47 and 204.50 ± 1.10 μA/mM for Hg(II), Cu(II), Pb(II) and Cd(II), respectively. The selectivity of the clicked-CoPc modified GCE toward Hg(II), Cu(II), Pb(II), Cd(II) present no interference from these metals ions. The fabricated electrochemical sensor exhibited very good electrochemical properties such as good reproducibility, stability, reusability and is suitable for the detection of heavy metal ions in tap water in our laboratory.

1. Introduction

The electrochemical sensors in the past decade represent the most rapidly growing class of chemical sensors for research or industrial applications [1–3]. They have a leading position among the presently available sensors that have reached the commercial stage. They have found a vast range of important applications in the fields of clinical, industrial, environmental and food monitoring. An electrochemical sensor provides low detection limit, high sensitivity, high surface area, good reproducibility, better signal to noise ratio and selective sensing of more than one metal ion [4,5]. These advances include the introduction of modified electrodes, the design of highly selective chemical recognition layers, of molecular devices or sensor arrays, and developments in the areas of microfabrication and flow detectors. The electrochemical method has been reported in literature for the detection of heavy metals but the modification steps of the electrode and the specific techniques employed have been (cyclic voltammetry (CV), open squart wave voltammetry (OSWV), differential pulse stripping voltammetry (DPSV) [6–9]. The working electrode can be modified using different methods to enhance the sensitivity, selectivity and reproducibility of the electrochemical sensor. In this work, the modification of the electrode was carried out via click chemistry which has been reported in literatures [10–16]. The difference between the reported click chemistry for modified electrode and this report is the chemical recognition molecule which is the metalphthalocyanine (MPc) complex and the analyte of interest. The metal phthalocyanines complexes have been used for organophosphorous pesticide detection as well as Quartz Crystal Microbalance (QCM) sensing as presented some literatures [17–19]; and for toxicology [20–25] which is different from this work where we employ a low symmetry metal phthalocyanine for selective detections of heavy metals such as (Hg(II), Cu(II), Pb(II) and Cd(II). Indeed, these metals can be harmful to human health even in small amounts. Lead and cadmium in the body can cause permanent damage to the central nervous system, the brain, and kidneys and has been implicated in human hypertension [26,27]. Copper is essential substance to human life, but chronic exposure to contaminant drinking water with copper can result in the development of anemia, liver and kidney damage [28,29]. Injection of mercury via drinking water can have harmful effects in the kidneys and brain [30]. Therefore, with this multiple harmful effect of the above metals in human health, there is a need of developing a novel sensitive material for their monitoring.

The synthesis of low symmetric alkynyl substituted cobalt tetrakis

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https://doi.org/10.1016/j.jelechem.2018.02.016
Received 30 October 2017; Received in revised form 29 January 2018; Accepted 6 February 2018
Available online 07 February 2018
1572-6657/