Electrooxidation of Chlorophenols Catalyzed by Nickel Octadecylphthalocyanine Adsorbed on Single-Walled Carbon Nanotubes

*Samson Khene, Tebello Nyokong**

Department of Chemistry, Rhodes University Grahamstown 6140, South Africa
Tel.: +27-46-603 8260; fax: +27-46-622 5109
*e-mail: t.nyokong@ru.ac.za

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Abstract
We described the synthesis of nickel octadecylphthalocyanine ($NiPc(C_{10}H_{21})_8$), followed by its adsorption on single-walled carbon nanotubes (SWCNT) to form SWCNT-$NiPc(C_{10}H_{21})_8$ conjugates. SWCNT-$NiPc(C_{10}H_{21})_8$ was used to modify a glassy carbon electrode (GCE) and for the electrooxidation of 4-chlorophenol and 2,4-dichlorophenol. The SWCNT and $NiPc(C_{10}H_{21})_8$ have a synergistic effect on each other in terms of improving electrocatalysis for the detection of chlorophenols. The stability of the electrode improved in the presence of $NiPc(C_{10}H_{21})_8$ or NiPc compared to the bare GCE. The presence of SWCNT improves the electrocatalytic behaviour of $NiPc(C_{10}H_{21})_8$ but not of unsubstituted NiPc. All modified electrodes showed improved stability towards the detection of 2,4-dichlorophenol. The best stability for 4-CP detection was observed in the presence of SWCNT for $NiPc(C_{10}H_{21})_8$.

Keywords: Nickel phthalocyanine, Single-walled carbon nanotubes, Cyclic voltammetry, Chlorophenol, Electrocatalysis

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1 Introduction

Chlorophenols constitutes a major class of organic pollutants that contaminate the ecosystem and accumulate in the food chain [1–3]. Rapid industrial and agricultural growth worldwide has led to further discharge of toxic substances such as chlorophenols as effluents. Chlorinated phenols such as 4-chlorophenol and 2,4-dichlorophenol are classified as priority pollutants by both the European Union (EU) and the United States Environmental Protection Agency (USEPA)[1,4,5]. Chlorinated phenols and in particular the polychlorinated phenols exhibit more resistance biotransformation in the environment than the monochlorinated derivatives [6,7]. Glassy carbon [8], platinum (Pt) [9–11] and gold (Au) electrodes [12] have been used for electrooxidation of chlorophenols but they showed instability towards electrode fouling.

Single-walled carbon nanotubes (SWCNT) have remarkable electrical, chemical, mechanical and structural properties and have found their applications in various disciplines, such as electrochemistry [13], material science [14] and surface science [15]. SWCNT are an ideal material to use in the fabrication of electrochemical sensors, because of their electrical conductivity, large surface area, low surface fouling and ability to reduce overpotentials [16–19]. It has been demonstrated that electrodes modified with SWCNT show enhanced sensitivity for detection of analytes [20–22]. Metallophthalocyanines (MPc) have been used to functionalize SWCNT, covalently [23] or noncovalently (π–π interaction) [24], in order to improve the electron transfer process, in electrocatalysis.

Electrooxidation of chlorophenols on glassy carbon electrode (GCE) modified with nickel based cyclam, porphyrin and tetrasulfonated phthalocyanine has been reported [25,26]. These complexes were found to reduce fouling of electrodes to different extents [25,27–29]. Hence in this work, the two electrocatalysts (SWCNT and MPc) are employed together with the aim of exploiting their combined activities towards the detection of chlorophenols. In this work $NiPc(C_{10}H_{21})_8$ is chosen since MPc containing long chain alkyl substituents were found to be better electrode modifiers than aryl substituents [30]. $NiPc(C_{10}H_{21})_8$ is adsorbed onto SWCNT via π–π interaction. It has been reported that during the oxidation of chlorophenols on electrodes modified with polymerized NiPc derivatives, the well known [29] extensive fouling of the electrodes by a layer of polymerized chlorophenol oxidation products is weaker on NiPc derivatives than on the bare GC electrode [27]. This was attributed to the high porosity of the polymerized chlorophenol layer, which allows the passage of chlorophenol molecules to the polyNiTSPc film [27]. Thus the aim of this work is to reduce fouling by using a combination of SWCNTs and a NiPc derivative containing bulky substituents. The combi-

