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β–Cyclodextrins incorporated multi-walled carbon nanotubes modified electrode for the voltammetric determination of the pesticide dichlorophen

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ABSTRACT

In this work, a glassy carbon electrode modified with β–cyclodextrins and multi–walled carbon nanotubes (β–CDs/MWCNTs/GCE) was constructed and applied for the square-wave adsorptive stripping voltammetric (SWAdSV) determination of the pesticide dichlorophen (*Dcp*). For the first time, this compound was electrochemically investigated. The voltammetric measurements were conducted in phosphate buffer (PBS) at pH 6.5 as a supporting electrolyte, and SWAdSV technique parameters were optimized. A linear calibration curve in the wide concentration range from 5.0×10^{-8} mol L^{-1} to 2.9×10^{-6} mol L^{-1} was obtained. Excellent analytical performance in terms of limit of detection (LOD) of 1.4×10^{-8} mol L^{-1} was achieved. The utility of the proposed method was verified by the quantitative analysis of *Dcp* in Pilica River water samples with satisfactory results. The characterization of modified electrodes was conducted by means of atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). Moreover, in this work, the dissociation constants (pK_a) of *Dcp* using potentiometric pH titration were estimated. The stoichiometry of the *Dcp*–β–CDs inclusion complex formed in solution was determined by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, and a binding constant (β_2) was estimated from NMR titration studies.

1. Introduction

The escalating demands for analyzing the environment led to the development of more selective and sensitive analytical systems. Great progress in the detection area can be achieved by applying nanotechnology [1]. As a matter of fact, nanomaterials have unique properties such as long–range order, high packing density, and large surface to volume ratio, thus, they may serve to be potentially useful in a newly created environmental applications [2]. As a result, the research in the field of the applications of carbon materials in the electrochemical sensors is still the in-thing due not only to the new exciting forms of carbons (tubes, fibers, single graphene layers), but also because of the great demands for sensing analytes with clinical, environmental or industrial interest [3]. Moreover, the electrochemical sensing approach has been extensively utilized in view of the fact that electrochemistry is low–cost technique and allows to sensitively analyze a lot of compounds, including pesticides. In addition, electrochemistry provides a great tool for analysis due to their simplicity, rapidity and accessibility [4].

So far, the most often used nanomaterials in electrochemistry are carbon nanotubes (CNTs), mainly single–walled carbon nanotubes (SWCNTs) and multi–walled carbon nanotubes (MWCNTs). CNTs consist of cylindrical graphene sheets of nanometer diameters, and they show unique properties, such as high electrical conductivity, high chemical stability, extremely high mechanical strength, and modulus [4]. Due to the fact that CNTs offer exceptional advantages, *i.e.* enhanced electronic properties, a large edge plane/basal plane ratio, and fast electrode kinetics, they have been successfully incorporated into electrochemical sensors. In addition, CNTs can increase the surface area of the electrode and its porosity, as well as act as a conductive pathway to the electrode. Therefore, sensors based on CNTs generally have a higher sensitivity, a lower detection limit, and faster electron transfer kinetics when compared to the traditional carbon electrodes [5].

Cyclodextrins (CDs) are a family of compounds which are made up of sugar molecules bound together in a ring (cyclic oligosaccharides). Due to its structure, they can form inclusion complexes with numerous molecules [6]. This unique property has led to the expansive applic-

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ability of the CDs in the pharmaceutical, chemical and food industries [7]. β–Cyclodextrins (β–CDs) are oligosaccharides consisting of seven glucose units, they are soluble in water and environmentally friendly, they can enhance the dispersibility and stability of the nanomaterials [8]. Electroanalytical applications of β–CDs are based on the formation of an inclusion complex, a biomolecular recognition and a selective preconcentration of analyte at the electrode surface. Thus, to date, β–CDs were widely used in electrochemical measurements when they were present directly in the supporting electrolyte solution with analyte [9–12], or when the modification of the electrode was performed using some of the common methods, such as Langmuir–Blodgett (L–B) technique [13], self–assembly method [14,15], formation of polymer films [2,16], preparation of carbon paste electrodes modified with cyclodextrins [17–19], and modification of the electrode surface with CDs and multi–walled carbon nanotubes composite [20].

When the CNTs are assembled with CDs, a new material simultaneously possess the unique properties of carbon nanotubes and cyclodextrins [21]. This provides an excellent opportunity for their applications as the electrochemical sensors. Up till now, electrodes modified with β–CDs incorporated multi–walled carbon nanotubes (MWCNTs) have been auspiciously applied to investigate various organic molecules due to the exceptional properties of both materials [22,23].

Nowadays, pesticides are frequently used in horticulture and agriculture to prevent, repel, and control pests. Although pesticides are generally favorable in farming, their use have also some drawbacks. A huge consumption of pesticides and their incompetent use have led to soil and water contamination. To reduce the harmful effects of pesticides, dosage controls and trace level monitoring are crucial. Thus, there is an essential need to develop novel, sensitive, selective and simple procedures for the determination of the pesticides with the lowest possible concentration ranges. Moreover, it should be emphasized that various kinds of functional groups are frequently present in the pesticide molecules, and the physical, chemical and ecotoxicological properties of pesticides are mostly related to their structures. In addition, the tendency of the pesticides to change their properties, when they are scattered in the fields, can be observed. It was found that one of the most crucial are the acid–base properties. The knowledge of the acidity constant (K_a or pK_a) of the pesticides is important in order to determine their behavior in the environment and to predict the nature of the species present in the environment (neutral molecule or a charged ion: a cation and/or an anion) [24].

The object of the research in this paper is a chlorophenolic compound, dichlorophen (*Dcp*, bis(5–chloro–2–hydroxyphenyl) methane, Fig. 1), which is utilized as a fungicide, germicide, and antimicrobial agent. *Dcp* is used for the control of mosses in amenity turf, golf greens and hard surfaces, liverworts and mosses on ornamentals, fruit trees in winter. It is also applied to control of fungal pathogens on glasshouses surfaces and in nurseries [25]. *Dcp* is also a veterinary fungicide used to prevent the tapeworm infections in dogs and cats, and it is very effective against many cellulolytic fungi [26]. Moreover, *Dcp* is commonly used as a bactericide and fungicide in a variety personal care product formulations (soaps, shampoos, toothpastes, mouthwashes, deodorants, foot powders, papers, adhesives, bandages and cooling fluids) [27].

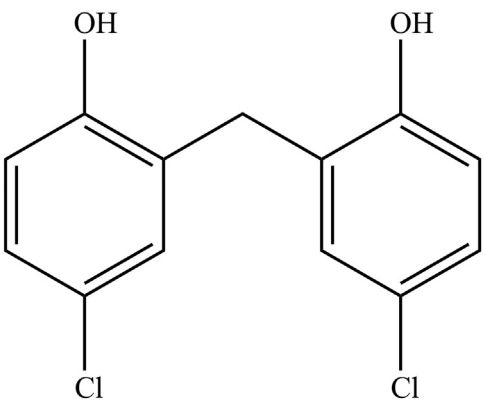

Fig. 1. Chemical structure of *Dcp*.

It was alleged that *Dcp* is very toxic to aquatic organisms, and can cause long–term effects in the aquatic environment. Because of its toxicity, restriction on the use of *Dcp* in cosmetic formulations has already been applied, and the current EU maximum authorized concentration for *Dcp* of 0.5% [28]. So far, the most frequently used methods for the determination of chlorophenols residues including *Dcp* have been chromatographic techniques [29–31] which need organic solvents. To the best of our knowledge, there is no information in the literature about the electrochemical behavior of *Dcp*. Thus, the voltammetric procedure for the determination of *Dcp* is reported for the first time in this work.

Taking into account the excellent electrochemical properties of MWCNTs and the favorable properties of β–CDs, the present work reports an approach based on the simultaneous modification of a glassy carbon electrode (GCE) with β–CDs and MWCNTs composite. The chemical recognition of *Dcp* by the application of β–CDs was connected with the advantage of a faster electron transfer process caused by the MWCNTs present at the electrode surface. Thus, the aim of our work was to develop a highly sensitive, selective, and stable electrochemical sensor based on the β–CDs and MWCNTs composite. Although, β–CDs incorporated MWCNTs modified glassy carbon electrode was prepared based on the similar methods described in the literature, the previously reported analyses were performed mainly using cyclic voltammetry (CV) [2–4,23], differential pulse voltammetry (DPV) [22,32–34], and square–wave voltammetry (SWV) [35,36]. In this paper, the modified electrode was amended by changing the amount of the components of the composite, and utilized for the square- wave adsorptive stripping voltammetric determination (SWAdSV) of *Dcp*. For the first time, *Dcp* was electrochemically investigated in this work, and the electrochemical mechanism of the β–CDs/MWCNTs/GCE for *Dcp* was also discussed. Special attention was given to the characterization of the β–CDs/MWCNTs/GCE by AFM, EIS and CV. In addition, the determination of the dissociation constants (pK_a) of *Dcp* by means of the potentiometric pH titration was performed. Moreover, the inclusion complex formation of β–CDs with *Dcp* was investigated by ^{1}H NMR spectroscopy, and the binding constant (β_2) was estimated from NMR titration studies.

2. Experimental

2.1. Reagents and materials

β–cyclodextrins (purity of 98%), multi–walled carbon nanotubes (95% purity, a diameter of 6–9 nm, and a length of 5 μm), and the analytical standard of *Dcp* (PESTANAL®, 98.61% purity) were obtained from Sigma–Aldrich (Poland). *Dcp* stock solutions (1.0×10^{-3} mol L^{-1} for CV, and 1.0×10^{-4} mol L^{-1} for SWAdSV) were prepared weekly in methanol as solvent (pa purity, POCh SA, Gliwice, Poland) and kept in a refrigerator when not using. The analytical standards of interfering agents were of analytical reagent grade, and the stock solutions concentration of interferents was 1.0×10^{-3} mol L^{-1}. Phosphate buffer solution (PBS) was used as the supporting electrolyte. Different pHs were obtained by mixing solutions of Na_2HPO_4 and KH_2PO_4 (both 1/15 mol L^{-1}). The solutions were prepared with triple distilled water. To polish GCE, alumina slurry (Al_2O_3, 0.3 μm, ATM GMBH, Germany) was used. Argon (5 N, Linde gas, Poland) was used without further purification. ^{1}H NMR measurements were carried out with the use of heavy water (D_2O, 99.8%, Sigma–Aldrich, Poland).

2.2. Instruments

A potentiostat EmStat^3 (Palm Instruments B.V., the Netherlands) in a conjunction with an electrode stand (type M164D, MTM Anko