CHAPTER I

INTRODUCTION

1.1 Introduction

The electrochemical applications of synthetic conductive diamond thin film electrodes have been increasingly reported [1-8]. Diamond is one of the nature's best insulators, however, when doped with boron the material can possess either semicoducting or semimatallic electronic properties depending on the doping level [9]. The growing popularity of this boron-doped diamond electrode in analytical applications over its conventional counterparts lies mainly on its various attractive properties, such as very low and stable voltammetric background currents, wide working potential window in aqueous solutions, high resistance to deactivation via fouling, insensitivity to dissolved oxygen and long-term response stability [10-12]. Therefore, boron-doped diamond (BDD) thin film electrodes have been emerged as a unique electrode material in many fields of electrochemistry, especially in the electroanalysis applications [12-15].

Recently, the construction of chemically modified electrodes (CMEs) capable of lowering the operational potential required to oxidize scarcely electroactive organic compounds has caught a great deal of interest. Reduced electrode fouling has also been reported. CMEs based on the modification of glassy carbon or graphite rods with various metals (e.g. copper [16-18], cobalt, and nickel [19-23]) have shown a catalytic activity towards polyhydroxy compounds. These electrodes have been successfully applied to detect carbohydrate [17, 19-21], amino acids [21, 23], sugars [16] and aliphatic alcohol compounds [23] using amperometric detection. However, glassy carbon electrode has a major drawback of providing high background current. It has been reported that a more stable and inert electrode with low background current can be obtained by depositing metal electrocatalysts onto the surface of this electrode [24]. These metal-modified diamond electrodes appear to be well suited to overcome such problems.

Moreover, the ion implantation has been successfully used in doping semiconductors such as silicon and gallium arsenide. Recently, applications of ion-implanted diamond have been of particular interest. In this study, the electrical conductivity and other physical properties can be controlled by ion-implanting diamond. Only a few applications for electrochemical use by metal-implanted conductive BDD electrodes have been reported [25, 26]. Therefore, we are interested in developing a method for the determination of tetracyclines by using the Ni-implanted diamond electrode.

Many antibiotics are widely used in veterinary for preventing and treating diseases as well as for promoting growth in food producing animals. These antibiotics are aminoglycosides, β-lactams, chloramphenicol, tetracyclines, macrolides, sulphonamides, quinolines, and nitrofurans. Tetracycline is one of the most important antibiotics that we are interested in this study. Tetracycline is a broad-spectrum antibiotic, which is commonly used in human pathologies as well as in veterinary medicine, animal nutrition and feed additives for cattle growth. It is used for many different infections, such as respiratory tract infections, urethritis and severe acne [26-28].It also plays a major role in the treatment of multidrug resistant malaria. Adverse effects include gastrointestinal disturbances, renal dysfunction, hepatotoxicity, raised intracranial pressure and skin infections, such as rosacea and perioral dermatitis.

Numerous methods have been reported for the determination of tetracyclines. These included titrimetric, spectrophotometric [29, 30], fluorimetric [31-33], chemiluminescence [34], liquid chromatographic [35] and electrochemical methods [36-39]. Among these, the electrochemical method is distinctly attractive owing to its simplicity, fast analysis, low cost and high sensitivity. There are several reports utilizing polarographic methods for the analysis of tetracycline[39]. Its major drawback is the use of mercury, which is toxic and is not practical for some applications, including the flow injection.

In the present work, boron-doped diamond (BDD) electrodes have been modified by nickel implantation. After the films were obtained, the sensitivity were compared with those of as-deposited BDD electrodes (i.e. unmodified BDD electrodes). The surface characteristics of Ni-implanted BDD and the as-deposited BDD were then investigated by optical microscopy and raman spectroscopy. We report the use of nickel-implanted boron-doped diamond thin film electrodes to study the electrochemical oxidation of tetracycline hydrochloride, doxytetracycline hydrochloride, chlortetracycline hydrochloride and oxytetracycline hydrochloride using cyclic voltammetry. The performance of the Ni-DIA electrode for the detection of tetracycline was examined by hydrodynamic voltammetry and FIA with amperometric detection for the determination of tetracyclines in commercially available capsules. In addition, the Ni-DIA was coupled to a HPLC system and its optimum operating potential, linear range, detection limit and repeatability for the determination of tetracycline hydrochloride, doxytetracycline hydrochloride, chlortetracycline hydrochloride and oxytetracycline hydrochloride in real samples were investigated.

1.2 Objective and scopes of the research.

The present work describes the development and application of Ni-implanted diamond electrodes for the electroanalytical study.

Boron-doped diamond thin film electrode (BDD) was initially prepared by chemical vapor deposition (CVD). The experiment was divided into topic of the electroanalysis of tetracyclines group using Ni-implanted boron-doped diamond electrode (Ni-DIA) applied to a flow injection system with high-performance liquid chromatography for quantitative determination of each component in shrimp.

The Ni catalysts were implanted onto a BDD electrode and its surface electrochemical characteristics were studied by optical microscopy and raman spectroscopy. The fundamental electrochemical properties of this Ni-DIA electrode were then investigated and compared with those of the BDD and glassy carbon electrodes by cyclic voltammetry. The conditions such as pH, scan rate and concentration of tetracycline have also been optimized.

In addition, the hydrodynamic voltammetry, linear range, detection limit and repeatability were studied with a flow system for the determination of tetracyclines in commercially available capsules. Finally, the Ni-DIA electrode was employed as a detector in a HPLC system for the determination of tetracyclines in shrimp samples and the results were validated and compared with those obtained by the AOAC standard method (HPLC with UV detector).