

**DEVELOPMENT OF A SENSITIVE ELECTROCHEMICAL SENSOR
BASED ON CARBON DOTS AND GRAPHITIC CARBON NITRIDE FOR
THE DETECTION OF 2-CHLOROPHENOL AND ARSENIC (III) IN
WATER**

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**This dissertation is submitted to Vaal University of Technology in
fulfillment of the requirements for the degree of Magister
Technologiae in Chemistry**

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February 2021

DECLARATION BY CANDIDATE

I hereby declare that the master dissertation titled “Development of a sensitive electrochemical sensor based on carbon dots and graphitic carbon nitride for the detection of 2-chlorophenol and arsenic (III) in water” submitted for M-Tech: Chemistry, at Vaal University of Technology has never been submitted to any other institution of higher learning. I further declare that all cited sources are acknowledged by list of referencing.

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THG Moundzounga

Vaal University of Technology (February 2021)

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DEDICATION

This master work is dedicated to my Family for their unconditional love, support, motivational talks and prayer.

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LIST OF PUBLICATIONS

The following manuscript will be published from this project:

Submitted manuscript

1. A nanocomposite of graphitic carbon nitride and carbon dots as a platform for sensitive voltammetric determination of 2-chlorophenol in water. Submitted to *International Journal of Electrochemical Science* (***under review***).

Manuscript under preparation

1. Electro-oxidation of sulfamethoxazole on a glassy carbon electrode modified with a composite of carbon dots and graphitic carbon nitride.
2. Voltammetric determination of As (III) in water using g-C₃N₄/CDs modified glassy carbon electrode.

ABSTRACT

The presence of organic and inorganic pollutants in aqueous environments is one of the major challenges confronting man. It is therefore important to develop sensitive, versatile and cheap techniques for their detection. Arsenic (III), 2-chlorophenol (2-CP) and sulfamethoxazole (SMX) are priority pollutants that pose health threats to humans and animals. This study was thus aimed at exploring two promising carbon nanomaterials as electrode modifiers for the electrochemical sensing of arsenic (III), 2-CP and SMX in water. Glassy carbon electrode (GCE) was modified with a nanocomposite of carbon dots (CDs) and graphitic carbon nitride (g-C₃N₄) and used as a sensor for the analytes in aqueous media. The CDs was prepared by a facile one-pot hydrothermal method using pine cone as the carbon source; g-C₃N₄ and g-C₃N₄/CDs nanocomposite were prepared via the microwave irradiation heating method. CDs, g-C₃N₄ and g-C₃N₄/CDs were dropped-dried on the surface of bare GCE. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the prepared materials. GCE, g-C₃N₄/GCE, CDs/GCE and g-C₃N₄/CDs/GCE electrodes were electrochemically investigated by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) using a ferrocyanide [Fe (CN) ₆]^{3-/4-} redox probe. The current and the reversibility of the redox probes were enhanced in the presence of modifiers. The electrochemical behavior of arsenic (III), 2-CP and SMX on different electrodes (GCE, CDs/GCE, g-C₃N₄/GCE and g-C₃N₄/CDs/GCE) were investigated by differential pulse voltammetry (DPV) under optimized conditions in a phosphate buffer solution (pH 7.6, 6 and 5 for 2-CP, As (III) and SMX respectively). The results demonstrated that the g-C₃N₄/CDs/GCE electrode significantly enhanced the oxidation peak current of all three analytes. The detection sensitivity of the analytes was greatly improved, suggesting that this new modified electrode has great potential in the determination of trace level of arsenic (III), 2-CP and SMX in water. The oxidation peak currents displayed a linear relationship to concentrations for 2-CP (0.5 - 2.5 μ M, $R^2=0.958$, $n=5$), arsenic (III) (2 - 10 μ M $R^2=0.978$, $n=5$) and SMX (0.3 - 1.3 μ M $R^2=0.9906$, $n=5$). The detection limits of 0.62 μ M, 1.64 μ M and 0.10 μ M were obtained for 2-CP, arsenic and SMX, respectively. Phenol and 4-chloro-3-methyl-phenol were found to interfere with the detection of 2-CP, while, Cu²⁺, Zn²⁺, Pb²⁺ and Cd²⁺ were the only significant ions that interfered with the electrochemical detection of arsenic (III). EDTA was used as a ligand to mask the interference effects of copper, cadmium,

lead and zinc on arsenic sensing. The modified electrode (g-C₃N₄/CDs/GCE) was used to determine arsenic, 2-CP and SMX in spiked tap and effluent water samples by the standard addition method and the results showed percentage recoveries varying from 93-118% for 2-CP, 98-100% for arsenic and 80-105% for SMX. The outcomes of this study established that the nanocomposite material represents an easy and sensitive sensing platform for the monitoring of arsenic (III), 2-CP and SMX in aqueous media.

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LIST OF ABBREVIATIONS

Abbreviations:

DPV	Differential pulse voltammetry
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
SWV	Square wave voltammetry
CDs	Carbon dots
g-C ₃ N ₄	Graphitic carbon nitride
CMEs	Chemically modified electrodes
WE	Working electrode
CE	Counter electrode
RE	Reference electrode
SEM	Scanning electron microscopy
TEM	Transition electron microscopy
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
EDS	Energy dispersive X-ray spectroscopy
HM	Heavy metals
CNTs	Carbon nanotubes
CNPs	Carbon nanoparticles

CPs	Chlorophenols
2-CP	2-chlorophenol
GCE	Glassy carbon electrode
PNEC	Predicted no effect concentration
EDTA	Ethylenediaminetetraacetic acid
EEC	Electric equivalent circuit
As	Arsenic
rpm	Revolutions per minute
SMX	Sulfamethoxazole
PBS	Phosphate buffer solution
PVP	Polyvinylpyrrolidone
PVA	Polyvinyl alcohol
CS	Chitosan

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CHAPTER 1

INTRODUCTION

1.1 Background

Water is an indispensable fluid which forms the streams, lakes and oceans. It is the predominant constituent of the fluids in living organisms and plays a crucial role in digestion, assimilation, elimination, and respiration (Liu et al., 2016a). Quality drinking water is vital to humans and animals even though it provides no calories or organic nutrients (Pacheco-Torgal and Labrincha, 2013). Rain water from the condensation of water vapor in the atmosphere, ground water, surface water, lake and river water are some of the purest forms of water sources. However, the release of untreated wastewater into the environment contaminates those water sources. Wastewater contains impurities which include harmful bacteria, antibiotics, oxides, aromatic pollutants such as chlorophenols, metal salts and heavy metals such as arsenic, selenium, lead, chromium, mercury, cadmium and copper (Dabrowski et al., 2004). The main sources of such water pollutants are diverse including textile, pharmaceuticals, mining, agriculture, paints, cosmetics, and photography industries. These industries produce, use and release organic and inorganic pollutants into the environment (Bhanjana et al., 2018). Water contaminants can be harmful to the environment and living organisms. Some metals such as lead, cadmium, copper, zinc, nickel and arsenic, occur naturally in the environment and are necessary for some physiological and biological reactions in plants and animals. However, if their concentrations exceed the permissible limits, they may have negative impacts on humans and the environment (Bhanjana et al., 2018).

Heavy metals are serious pollutants in the environment and can enter the food chain via different means. Heavy metal ions can accumulate in the living body and cause diseases by bonding strongly with protein molecules in living cells (Kim et al., 2016). Their wide distribution, high toxicity and persistence, make them a group of significant pollutants (Dali et al., 2018). Heavy metals are non-degradable and are deposited into water sources through several channels such as mining related

activities, smelting, chemical, metallurgical industries, agriculture, waste disposal and pulp industries (Zaib et al., 2015; Olayiwola, 2016).

Lead, arsenic, mercury, cadmium, and copper are the most harmful metal ions and their impact on living organisms is life threatening (Deshmukh et al., 2018). Among the various heavy metals in nature, arsenic is of great concern due to its serious toxicity (Kim et al., 2016). The recommended guideline value set by the World Health Organization (WHO) for arsenic in drinking water is 10 µg/L (10 ppb) (WHO, 2011; Tiwari and Lee, 2017). Food, water and air are channels through which exposure to arsenic can occur. Arsenic can be found alone as a metal or as metal like compounds. It exists in four different oxidation states which are arsenate, arsenite, arsenic and arsine (+5, +3, 0, -3, respectively) under different conditions (Zaib et al., 2015; Olayiwola, 2016). Organic forms of arsenic are less harmful than inorganic arsenic. Inorganic arsenic displays extreme toxicity (Saha et al., 2017). The toxicity of arsenic varies greatly according to its oxidation state. For example, As (III) is far more toxic than As (V) because it reacts with enzymes of human metabolism (Morillo et al., 2015). Continuous exposure to arsenic may lead to vitamin A deficiency which is related to night blindness, heart diseases, hypertension, and many other diseases such as cerebrovascular diseases, headaches, convulsion, drowsiness, pigmentation, vomiting, blood in the urine, loss of hair, stomach pain, cramping muscles and cancer (Abdul et al., 2015). Drinking arsenic contaminated water as low as 0.17 ppb over a period of time may result in a range of serious health issues, among them skin itching when under the sun, burning and watering of eyes, weight loss, loss of appetite, weakness, melanosis, keratosis, leucomelanosis, and lethargy which limits physical activities and working capacities of individuals (Saha et al., 2017). Therefore, detection of arsenic in drinking water is of great importance and has become a focus during the last decade (Saha et al., 2017). In ground water, many forms of arsenic compounds are present, but the predominant ones are arsenic (III) and (V) and a minor amount of methyl and dimethyl arsenic compounds. Those found in water are arsenic H_2AsO_3^- , arsenate H_2AsO_4^- , methyl arsenite, dimethyl arsenite and dimethyl arsenate (Spallholz et al., 2004).

The presence of harmful organic substances in water can also have debilitating effects on human health and animals. Among these are the pharmaceutical pollutants which have been labelled as emerging organic pollutants (Miller et al., 2018). The main classes of pharmaceuticals found in environmental samples and wastewaters include antibiotics, antipyretics, analgesics, anti-

inflammatories, antimicrobials and hormones (Feier et al., 2018). The world's largest production of pharmaceutical drugs are antibiotics, which play an important role in the treatment and prevention of infections caused by microorganisms such as bacteria and certain parasites. Additionally, antibiotics are commonly utilized in farming and husbandry for product enhancement, growth promotion and prevention (Kokulnathan and Chen, 2020). Antibiotics and their bioactive metabolites are continuously introduced into the aquatic systems at lower levels (ng/L or pg/L) (Feier et al., 2018).

The presence of antibiotics in the environment can be attributed to multiple factors including the release of unabsorbed antibiotics by animals and humans into the water stream. Moreover, laboratories, factories and medicinal practices discard unused antibiotics and they find their way into water sources. Their existence at very low levels in the environment can have a harmful and deleterious impact on humans and ecosystem (Mahmood et al., 2019). The risks that are posed by the presence of antibiotics in water has gained more attention, because it may lead to the development of antibiotic-resistant bacteria in nature (Mahmood et al., 2019).

Sulfamethoxazole (SMX) is one of the numerous antibiotics which belongs to the sulfonamide family (Le et al., 2020). Sulfonamides are bacteriostatic which means they inhibit the growth of bacteria but do not kill them (Alkhawaldeh, 2020). Sulfamethoxazole is an important antibiotic which is often prescribed for the treatment of several bacterial infections such as intestinal infections, middle ear and respiratory infections in combination with trimethoprim (at a fixed ratio of 5:1) under the brand name Bactrim (Salmanpour, 2019). It is also used as a food additive in livestock production (Misal et al., 2020). In many countries, SMX is the most frequently detected sulfonamide in various water resources (Misal et al., 2020). Based on the no observed effect concentration (NOEC) of the most sensitive organisms, the predicted no effect concentration (PNEC) of 520 ng/L of SMX in effluent is set as a standard limit (Straub, 2016). Continuous consumption of sulfamethoxazole can lead to shortness of breath, headache and rapid heart rate. The determination of sulfamethoxazole could be useful for controlling the drug dose in humans (Sgobbi et al., 2016). The exposure of microbial communities to SMX in water sources can result in antibiotic resistance (Zhang et al., 2009), which can cause adverse health effects by decreasing the ability of antibiotics to treat bacterial infections (Misal et al., 2020). Therefore, a sensitive,

stable and reliable detection method is needed to monitor the residues and metabolites in aquatic environments (Zhang, 2019).

Another class of harmful organic contaminants which have been detected in surface and ground waters are the phenolic compounds. Of the phenolic compounds, chlorophenols (CPs) are notorious for their adverse health effects (Gan et al., 2017). CPs are generated by replacing hydrogen atoms in the phenol molecule by chlorine atoms (Kuśmierek and Świątkowski, 2015). CPs can be introduced into the water, air and soil from various sources such as wood and fiber preservatives, production of pesticides and their use (Kuśmierek and Świątkowski, 2015). They are released into the environment as products of metabolic degradation of chlorinated pesticides, and then result as byproducts of the chlorination of drinking water (Lia et al., 2013). Most of the chlorophenols are considered as high priority pollutants even at low levels, including 2-chlorophenol, 2,4-dichlorophenol, 4-chlorophenol, 2,4,6-trichlorophenol, 3,5-dichlorophenol, and 2,3,4,5,6-pentachlorophenol (Kuppusamy and Jayadevan, 2015).

As a consequence, the US Environmental Protection Agency and the European Union has listed the above phenols as priority pollutants and regulated their maximum permissible concentration in drinking water at 0.5 ng/mL (Lia et al., 2013). Some chlorophenols are considered as carcinogens (e.g. 2-chlorophenol) and some are recognized as endocrine disruptors (Zhenga et al., 2018). Therefore, development of methods for the detection of CPs is a worthwhile endeavour (Liang et al., 2016). CPs can accumulate in the human body and result in many negative effects which include carcinogenicity and acute toxicity (Ya et al., 2018); they can also cause itching, fainting, anemia, comedones even at low level concentrations (Liang et al., 2016). Due to their high toxicity, strong odor emission, persistence in the environment and suspected carcinogenetic and mutagenic properties, chlorophenols are duly recognized as hazardous substances (Zhenga et al., 2018). The development of simple, sensitive, reliable and rapid detection methods for 2-chlorophenol is therefore important (Ya et al., 2018).

Various methods have been developed in chromatographic and spectroscopic domains to monitor water pollutants including heavy metals, pharmaceuticals, and chlorophenols. These methods can be very sensitive and accurate. However, they do have some drawbacks which include high cost and complexity of analytical equipment, non-portability of the equipment and tedious sample preparation process amongst others (Ikhsan et al., 2016). As a result, it is necessary to develop

alternative methods in which these drawbacks are circumvented. In this regard, electrochemical devices offer simple, inexpensive and rapid means for the determination of electrochemically active organic pollutants in aqueous media. It is worth mentioning that electrochemical sensors are also well suited for onsite analysis because of their small sizes. In fabricating an electrochemical sensor, the sensing platform (i.e. the electrode surface) can be designed to maximize communication between the analyte and the sensor. In this way, high sensitivity and considerable selectivity can be achieved (Peleyeju et al., 2017). The modification of the surface of commercial electrode such as the glassy carbon electrode (GCE) to obtain enhanced signal when used to analyse pollutants has been the subject of many scientific reports. Materials possessing nanometric dimensions have been used as modifiers to achieve this goal. The choice of nanomaterials is often informed by their beneficial properties including electrical conductivity, high surface area, catalytic activity, and so on. Some of the materials also have functionalities that promote interaction between the target pollutant and the modified electrode. Carbon nanomaterials, metal and metal oxide nanoparticles (Keivani et al., 2017), nanofibres, etc. have been explored as electrode modifiers to detect and quantify various analytes in water.

Recently, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a polymeric material comprising mainly carbon and nitrogen atoms, has been receiving attention as a promising material for electrochemical applications. It has been indicated to have sites that may mediate redox processes (Liu et al., 2016b; Vinoth et al., 2020). Liu et al. (2018) reported the non-enzymatic determination of glucose using a composite electrode modifier containing $g\text{-C}_3\text{N}_4$. The authors suggested that the presence of $g\text{-C}_3\text{N}_4$ promotes the accumulation of the glucose molecules on the surface of the electrode. This accumulation can lead to improved electrochemical signals. Tian et al. (2017) also prepared a bi-component electrode modifier with $g\text{-C}_3\text{N}_4$ and reported that the sensing platform exhibited considerable catalytic activity for H_2O_2 . The stability of $g\text{-C}_3\text{N}_4$ in high adsorption capacity are beneficial for electroanalysis. The abundant pi bonds in the polymeric material may also offer benefits in the determination of organic pollutants. Its low conductivity, however, is a disadvantage (Luo et al., 2019). Thus, most electrochemical investigations in which $g\text{-C}_3\text{N}_4$ is used as electrode materials/modifiers, have incorporated other materials which can enhance conductivity (Rajkumar et al., 2018; Rajput, 2020).

In this study, a composite of g-C₃N₄ and carbon dots (CDs) was prepared and used as an electrode modifier. Carbon dots are a stable and electrically conductive carbon materials whose sizes are below 10 nm. They have been reported as having excellent electrocatalytic properties and thus have been employed in a variety of electrochemical studies. It was thought that a sensing platform consisting of g-C₃N₄ and carbon dots (CDs) would be markedly sensitive to arsenic, SMX and CPs in aqueous solutions, and produce reproducible current signals which could be correlated to the amounts of the analytes in solution.

1.2 Problem statement

The need to monitor water pollutants has been justified in previous paragraphs. This section is just a summary of the problem that will be addressed in this study.

Arsenic, sulfamethoxazole and 2-chlorophenol are dangerous pollutants and their amounts in the aquatic environments have increased significantly because of the increase in mining, industrial and urban activities. Long term exposure to low doses of arsenic, 2-chlorophenol and sulfamethoxazole can lead to serious health issues. As a result, there is a great need to develop sensitive sensors for detection of these compounds in water. Among many techniques available to monitor water pollutants, electrochemical techniques have an advantage over the other techniques because of the low cost of the instrument, minimum sample preparation, faster analysis time and potentially high sensitivity. However, the electrochemical sensing platform (electrode surface) in most cases are not sensitive enough to detect the analytes. Therefore, there is a need for the detection limits to be improved by modifying the working electrode surface with materials that possess desirable properties.

1.3 Aims and Objectives

1.3.1 Aim of the study

The aim of this work was to develop a sensitive electrochemical sensor using a nanocomposite of graphitic carbon nitride and carbon dots as an electrode modifier for the determination of arsenic (III), 2-chlorophenol and sulfamethoxazole in water.

1.3.2 Objectives

The objectives of this work are as follows:

1. To synthesize graphitic carbon nitride (g-C₃N₄), carbon dots (CDs) and g-C₃N₄/CDs nanocomposite.
2. To characterize the g-C₃N₄, CDs and g-C₃N₄/CDs nanocomposite using TEM, XRD and FTIR.
3. To modify glassy carbon electrode (GCE) with g-C₃N₄, CDs and g-C₃N₄/CDs nanocomposite.
4. To characterize the original and modified electrodes using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).
5. To investigate the modified electrodes for the detection of arsenic (III), 2-chlorophenol and sulfamethoxazole using differential pulse voltammetry (DPV).
6. To apply the developed sensor to detect arsenic, 2-chlorophenol and sulfamethoxazole in real water samples.

1.4 Thesis Outline

This thesis is presented in seven chapters:

- Chapter 2 introduces organic pollutants and its associated problems when exposed to the environment. The current electrochemical detection techniques employed such as electrochemical impedance spectroscopy. Types of electrodes, factors affecting the current signal. Also, the chapter describes the sensors and various electrochemical sensors with specific attention given to sensor applications. The nature of the topic has been adequately interpreted in this chapter, and the literature discussed gave good insight into the problem at hand.
- Chapters 3 describes the materials and methodologies used in the preparation of the nanomaterials; instrumentation employed in the characterization of the sensor platform as well as the detection of arsenic, sulfamethoxazole and 2-chlorophenol.
- Chapter 4 contains results and discussion on the electrochemical detection of 2-chlorophenol in water using carbon dots-graphitic carbon nitride as modifier on the surface of glassy carbon electrode.
- Chapters 5 details the results and discussion on electrochemical detection of arsenic (III) on carbon dots-graphitic carbon nitride modified on glassy carbon electrode and deals also with interference challenges in the electrochemical detection of As (III) using complexometric masking approach.
- Chapter 6 features the results and discussion on electrochemical detection of sulfamethoxazole using carbon dots-graphitic carbon nitride modified glassy carbon electrode.
- Chapter 7 presents the general conclusion, and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter gives a broad view of chapter one. The principal focus of this review is on water pollution and the role of electrochemistry in monitoring organic and inorganic pollutants in water. The concepts in this review can be summarized as follows:

- The effects of water pollution
- Water pollutants and ways they can be monitored
- The efficacy of electrochemistry in environmental analysis
- Modified electrodes as electrochemical sensors

2.2 Water pollution

Among the various known forms of pollution, water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Indeed, it is a part of life itself, since the protoplasm of most living cells contains about 80% of water. However, years of increased industrial, agricultural and domestic activities have resulted in the generation of a large amount of wastewater containing a number of toxic pollutants, which are polluting the available fresh water continuously (Bhatnagara and Minochab, 2006). Many forms of impurities (pesticides, fertilizers, heavy metals, dyes and antibiotics), while contributing to the pollution of water, can also act as carcinogens when present above the permissible limits. The main sources of such pollutants include textile, pharmaceuticals, paints, cosmetics, and photography industries (Bhanjana et al., 2018). Due to the concern of pollutants on human and animal life, pollution control and management is now a high priority area. The availability of clean water for various activities is becoming the most challenging task for researchers and practitioners

worldwide (Bhatnagara and Minochab, 2006). In recent years, there has been an increasing interest in finding innovative solutions for the efficient detection and removal of contaminants from water.

2.2.1 Inorganic pollutants

Inorganic pollutants are pollutants obtained from mineral origin which are not produced by living organisms. Common inorganic pollutants includes metals and their salts, inorganic fertilizers, sulphides, acids, base and heavy metals. Inorganic pollutants such as heavy metals occur naturally in the environment and are necessary for various physiological and biological reactions in plants and animals. But beyond acceptable limits, they can become harmful for humans and the environment (Bhanjana et al., 2018). Heavy metal ions (HMI) are one of the micro pollutants that represent a growing environmental problem and have affected various components of the environment including terrestrial as well as aquatic biota. The principal sources of these heavy metal ions are cosmetics and their by-products, fertilizers and other chemicals generated from industrial or household waste (Bansod et al., 2017). HMI do not decompose and have a tendency to accumulate in living organisms, causing various diseases and disorders to the nervous, immune, reproductive and gastrointestinal systems. Once released into the environment, they continue to exist for decades or even centuries as they are non- biodegradable (Bansod et al., 2017). Among various heavy metals in nature, arsenic (III) has been of great concern due to its serious toxicity. Long-term exposure to inorganic arsenicals may cause many health problems such as skin lesions, cardiovascular diseases, and cancer (Duoc et al., 2020). As (III) has been selected as the inorganic pollutant to be detected in this study.

2.2.2 Organic pollutants

Water contaminants are generally classified as inorganic toxic elements, organic chemicals and microorganisms. The typical organic pollutants in water include pharmaceuticals, personal care products, endocrine disruptors, pesticides, organic dyes, detergents, and common industrial organic wastes like phenolics, halogens and aromatics (Lu and Astruc, 2020). Dense organic pollution of the environment becomes a dangerous threat to the health of life and the environment. Consequently, this calls for the development of novel advanced technologies to detect and remedy water pollution (Lu and Astruc, 2020). The determination of phenol derivatives is of high priority in environmental ground, and surface water, due to their inherent toxicity. Some of them may

cause danger to health and contribute to environmental pollution (Ozoner et al., 2011). Chlorophenols (CPs) are organic chemicals widely used in industry for the manufacturing of insecticides, herbicides, fungicides, biocides, as well as dyes. CPs such as 2-chlorophenol (**Figure 2.1**), 2,4,6-trichlorophenol, 2,4-dichlorophenol, are the most toxic and carcinogenic (Dong and Huajie, 2006). CPs can be either toxic or common microorganisms can be resistant to it. Inhalation and dermal exposure to CPs can cause irritation of the skin, eyes and mucous membranes in humans. It is also considered very toxic to humans through oral exposure. The ingestion of one gram has been reported to be lethal, with symptoms such as muscle weakness and tremors, loss of coordination, paralysis, convulsions and respiratory arrest (Fernández et al., 2013). Due to the low contamination level and severe toxicity of 2-chlorophenol, there is a need to develop a sensitive, simple and reliable analytical methods for its detection (Shi and Zhu, 2011). 2-chlorophenol is a representative of chlorinated compounds and is electrochemically active (Dong and Huajie, 2006). Electrochemical methods for the determination of 2-chlorophenol have been reported (Lia et al., 2013; Maochao Wei et al., 2014; Zhu et al., 2018).

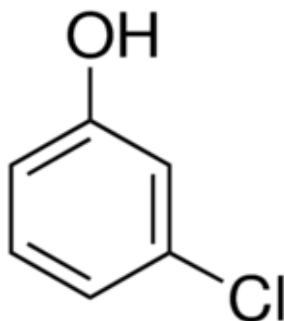


Figure 2. 1 Chemical structure of 2-chlorophenol (Gmurek et al., 2012)

In the aquatic environment, the presence of pharmaceutical substances and their possible effects on living organisms are a growing concern (Chang et al., 2008). Sulfamethoxazole (**see Figure 2.2**), is an antibacterial agent that is used to treat bacterial infections (Khanfar et al., 2020). The formulation of Sulfamethoxazole (SMX) is an important progress in the development of antimicrobial agents (antibiotics). SMX is one of the most active pharmaceutical ingredients of the antibiotics that are usually used in the treatment of urinary tract infection, chronic bronchitis, and

meningococcal meningitis. However, residues of sulfamethoxazole can cause severe food safety and environmental problems. Due to the increasing frequency at which SMX is prescribed, there is a continuous demand to develop new analytical techniques for their accurate determination (Khanfar et al., 2020). Electrochemistry, due to its fast response, simplicity and low cost of electrochemical analysis have found more popularity compared to other techniques for drug analysis in recent years (Salmanpour, 2019).

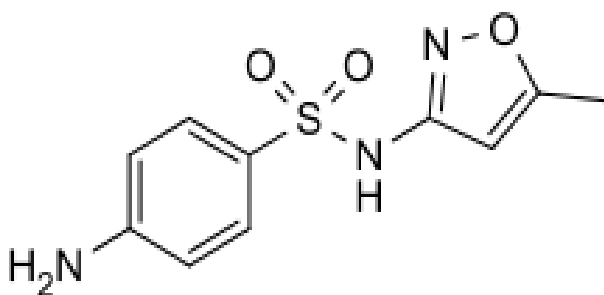


Figure 2. 2 Chemical structure of Sulfamethoxazole (Misal et al., 2020)

2.3 Electrochemical techniques for the determination of pollutants in water

Various methods have been reported for arsenic, 2-chlorophenols and sulfamethoxazole detection. Despite displaying good sensitivity and excellent selectivity, these methods have some drawbacks including high analytical cost, the requirement of expensive and complicated instruments, (Bhanjana et al., 2018). Therefore attention has shifted to electrochemical techniques for the monitoring of inorganic and organic contaminants from waste waters even if they are at low concentrations. Electrochemistry is about the relationships between chemical reactions and electricity. Techniques employing electrochemistry principles have an advantage over other techniques because they offer cheap and efficient ways of dealing with common pollutants including heavy metals and organic pollutants in the environment such as those of interest in this study (Oyagi, 2017). Electrochemical techniques are powerful and have found utility in the metal, pharmaceutical, food and beverage industries as well as environmental applications. They offer multiple advantages such as high sensitivity, selectivity, rapid analysis times, reduction in solvent

and sample consumption as well as ease of use and low operating costs. Based on this, electrochemical methods are considered very promising techniques in the endeavour for environmental monitoring and protection (Boikanyo, 2015).

Analytical electrochemistry is an area of electrochemistry which deals with the measurement of electrical quantities such as potential, current, or charge and their relationship to chemical reactions. Such electrical measurements have found many applications in environmental monitoring and industrial quality control. Electro-analytical techniques are based on an electrochemical process that occurs at the electrode-solution interface (Kolliopoulos, 2014). The electrochemical process requires a system of at least two electrodes (conductors) and a contacting sample (electrolyte) solution, which constitute the electrochemical cell. Electrochemical cells can be either galvanic or electrolytic cells. In galvanic cells, chemical energy is converted into electrical energy by a spontaneous chemical reaction at the electrodes of the cell. In electrolytic cells, electrical energy from an external source, is converted into chemical energy at the electrodes where a non-spontaneous chemical reaction occurs (Kolliopoulos, 2014).

Electrochemical techniques for the detection of analytes in an aqueous solution are classified based on the different electrical signals which are generated in the solution due to the presence of analytes. The presence of analytes can cause changes in several electrical parameters such as current, voltage, electrochemical impedance and charge. Based on various electrical signals, electrochemical techniques can be classified into four categories:

- Voltammetry/Amperometry
- Potentiometry
- Impedance measurement
- Coulometry

In these techniques, either one of the current or potential is controlled to measure the change in the other parameter (Bansod et al., 2017).

Table 2. 1 Classification of electroanalytical techniques according to the measured and controlled parameters (Kolliopoulos, 2014)

Measured parameter	Controlled parameter	Technique
M		
E	$i = 0$	Direct Potentiometry
E	$i = \text{stable}$	Potentiometric titrimetry
$E = F(t)$	$i = \text{stable}$	Chronopotentiometry
R or $1/R$ (G)	$E, f = \text{stable}$	Conductometry
$Z = F(f)$	$E = \text{stable}$	Impedance Voltammetry
w	$i = \text{stable}$ or $E = \text{stable}$	Electrogravimetry
$i = F(E)$	$E = F(t)$	Voltammetry (general)
$i = F(E)$	$E = F(t)$ (DMC)	Polarography
i	$E = \text{stable}$	Amperometry
$i = F(t)$	$E = \text{stable}$	Chronoamperometry
Q or $\int_0^t i dt$	$E = \text{stable}$	Potentiostatic Coulometry
Q or it	$E = \text{stable}$	Amperostatic Coulometry
$Q = F(t)$	$E = \text{stable}$	Chronocoulometry

E = electrode potential, f = frequency, F = function of the parameter, G = conductivity, i = electric current, R = resistance, w = mass of deposition, Z = impedance, DMC = Dropping Mercury Electrode and t = time.

2.3.1 Potentiometry

Potentiometric methods of analysis are based on measuring the potential of an electrochemical cell without drawing appreciable current. The two major types of analytical techniques in potentiometry are direct potentiometry and potentiometric titrations. In direct potentiometry, the cell potential is determined and related to the activity or concentration of the individual chemical species. In potentiometric titration the variation in cell potential is monitored as a function of the volume of reagent added (Isaac, 2011).

2.3.2 Coulometry

Coulometry is an electroanalytical method which involves the measurement of the quantity of electricity (in coulombs) needed to convert the analyte quantitatively to a different oxidation state. There are two general techniques that are used for coulometric analysis: controlled-potential (potentiostatic) and controlled-current (amperostatic) coulometry. In controlled-potential coulometry, the potential of the working electrode is maintained at a constant level. Controlled-current coulometry uses a constant current, which passes through a cell until an indicator signals the completion of the analytical reaction (Isaac, 2011).

2.3.3 Electrochemical Impedance measurement (EIS)

EIS technique is widely employed to study the interfacial properties of modified electrodes. It was also proven to be an efficient tool for recognition of appropriate interface properties that could be applied successfully in sensing. EIS describes the response of a circuit to an alternating current or voltage as a function of frequency. This technique serves as an inexpensive and simple technique for sensitive detection of toxic metal ions in biological and chemical matrices as compared to other electro analytical techniques. In EIS, an electrochemical reaction that takes place in an electrolytic cell is represented in terms of an electrical equivalent circuit (EEC). The current flowing in an electrified interface due to an electrochemical reaction leads to charge transfer along the electrified interface that further generates both faradaic and non-faradaic components (Bansod et al., 2017).

2.3.4 Voltammetry/Amperometry

Voltammetry is an electroanalytical technique which is based on the measurement of the current flowing through the working electrode dipped in a solution containing electroactive compounds, while a potential scanning is imposed on it. The potential is varied in some systematic manner to cause oxidation or reduction of the electroactive chemical species at the electrode. The resultant current is proportional to the concentration of the electrochemical species (Isaac, 2011).

Amperometry is a voltammetric technique, which is based on the measurement of current at a fixed operating potential. If this potential is conveniently chosen then the magnitude of current is directly proportional to the concentration. This current results from electrochemical oxidation or reduction of the electroactive compounds. Additionally, if steady state convection is employed, as in flowing streams and the concentration of electroactive species is uniform, then a constant current is measured (Isaac, 2011).

By varying potential, voltammetry gives information about an analyte under investigation by measuring current. There are many ways the potential is varied. The different ways of varying the potential have resulted in many forms of voltammetry such as cyclic voltammetry (CV), difference pulse voltammetry (DPV) and square wave voltammetry (SWV) (Oyagi, 2017). Among the various voltammetric techniques, cyclic voltammetry and difference pulse voltammetry are employed in the present work.

2.3.4.1 Cyclic voltammetry (CV)

In electrochemistry, CV is one of the most widely used voltammetric techniques. In CV, the working electrode is subjected to a triangular potential sweep whereby the initial potential (E_i) rises to a final potential (E_f) and returns to the start potential at a constant potential sweep rate. The current density is plotted against a function of applied potential and is obtained as a resultant voltammogram. Depending on the nature of the electroactive species, an oxidation or reduction peak is obtained on a cyclic voltammogram. The Parameters that are used to characterise CV, includes peak potentials and peak currents since they both give basic information for the diagnosis

quality of CV. The peak current for a reversible system is given by the Randles-Sevcik equation (Olayiwola, 2016).

$$i_p = 2.69 \times 10^5 n^{3/2} v^{1/2} D^{1/2} A C$$

Where i_p = peak current, n = number of electrons, A = area of electrode (cm^2), C = concentration (mol/cm^3), D = Diffusion coefficient (cm^2/s), V = scan rate (V/s).

The current corresponding to the oxidation/reduction is a characteristic signal of the analyte and is proportional to its concentration. Peak height and width of the voltammogram depends on the electrolyte concentration, nature of the electrode material and potential sweep rate. Applying this principle, sensors for various analytes have been developed (Theresa, 2015).

2.3.4.2 Differential pulse voltammetry (DPV)

DPV can be considered as a derivative of linear sweep voltammetry or staircase voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep or stair steps. The current is measured immediately before each potential change, and the current difference is plotted as a function of potential. The current changes between the working electrode and auxiliary electrode before and after the pulse sampled and their differences are plotted versus potential. These measurements can be used to study the redox properties of extremely small amounts of chemicals because of the following features:

- (1) In these measurements, the effect of charging current can be minimized and so higher sensitivity is achieved.
- (2) Only faradaic current is extracted and electrode reactions can be analyzed more precisely.

Some of the most important qualities of differential pulse voltammetry are based on the fact that reversible reactions show symmetrical peaks and irreversible reactions show asymmetrical peaks. The peak current is proportional to the concentration and the detection limit is about 10^{-8} M (molar). DPV is more sensitive than CV (Olayiwola, 2016).

2.4 General experimental setup for electrochemical detection

The general experimental setup for electrochemical detection of an analyte usually consists of an electrolytic cell consisting of an ionic conductor (an electrolyte) and an electronic conductor (an electrode). In this case, an aqueous solution consisting of the analytes, acts as the electrolyte solution. The cell potential is measured at the interface of the electrode and electrolyte solution. Various half reactions take place in the electrolytic cell and one of the half reactions of interest is usually at the working electrode (WE). The other electrode with respect to which the cell potential is measured is termed as reference electrode (RE). A general electrochemical experiment uses an external power supply to provide an excitation signal and measures the response function in the chemical solution considering the various system variables that are kept constant. For a three electrode cell arrangement, the third electrode is referred to as the counter electrode (CE). The current is usually passed between the WE and CE. A general three electrode cell setup for electrochemical detection of analytes in aqueous solution is represented in **Figure 2.3**. These electrodes are connected electrically to an electrochemical workstation that is basically laboratory equipment or portable in-field devices embedded with inbuilt power source for providing excitation signals to the electrode setup. The electrochemical workstation is connected to a computer installed with the required software platforms to interpret and analyze the data received from the experiment (Bansod et al., 2017).

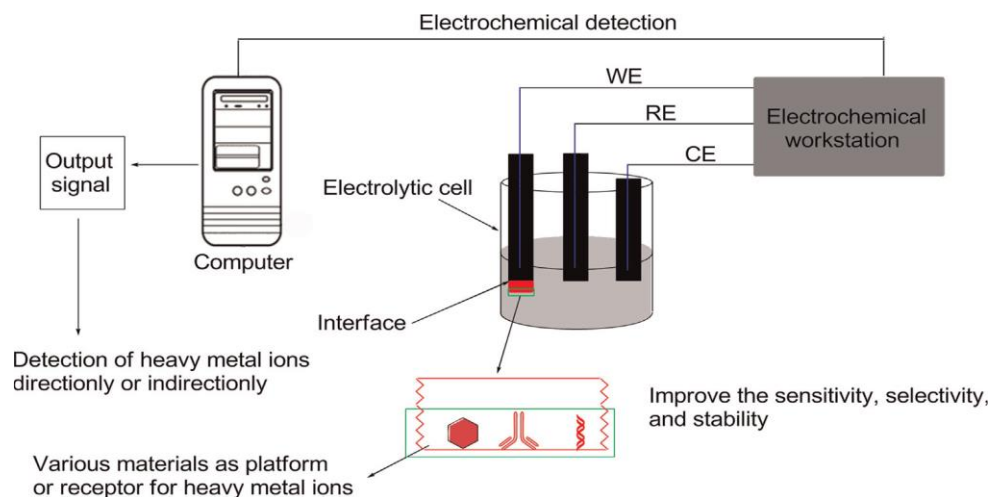


Figure 2. 3 Schematic illustration of general principle of electrochemical sensing of analytes
(Cui et al., 2015)

2.5 Type of Electrodes

Electrochemical experiments for potentiostatic measurements and techniques such as cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) are performed using a standard three electrode cell. This involves the use of a working electrode (WE), reference electrode (RE) and counter electrode (CE) which are connected to a potentiostat.

2.5.1 Working electrode (WE)

The WE serves as an electrochemical sensor and consists of a conducting substrate which had been modified to improve the sensing of a particular analyte (Lynn, 2013). The working electrode (WE) is the electrode in which the targeted electrochemical changes occur and where reaction of interest occur. Examples include mercury (Hg), Platinum (Pt), Palladium (Pd), Gold (Au) and Carbon electrode (Oyagi, 2017).

2.5.2 Reference electrode (RE)

Reference Electrode (RE) is the electrode that maintains a constant potential irrespective of the amount of current, if any, that is passed through it (Oyagi, 2017). It is the reference point against which the potential of other electrodes can be measured. The most common primary reference electrode is the Standard Hydrogen Electrode (SHE). But due to the difficulty in constructing and maintaining the SHE, a secondary reference electrode (Ag/AgCl, Calomel electrode) is preferred in voltammetric measurements. The Ag/AgCl electrode is composed of an Ag wire immersed in a solution saturated with AgCl and KCl (Theresa, 2015).

2.5.3 Counter electrode (CE)

The Counter electrode permits the passage of current in an electrochemical reaction through it without disturbing the potential of the reference electrode. The Platinum electrode is often the best choice in this regard due to its inertness and speed with which most electrode reactions occur at its surface (Theresa, 2015). The CE balances the current generated at the working electrode. For example, if an oxidation reaction occurred at the WE, the opposing reduction reaction occurs at the CE. In general, the potential is measured between the WE and RE and the current is measured between the WE and CE (Theresa, 2015).

2.6 Factors defining the measured current

Electrochemically redox reactions involve electroactive species. In a controlled-potential technique, in which the potential of the working electrode allows the half reaction of the electroactive species to take part, the measured current is governed by the factors below:

- The rate of the mass transport with which the electroactive species are transferred to the electrode's surface in order to replenish the species that has already reacted and maintain the faradaic current.
- The rate of the electron transfer across the interface.

- The rate of other different chemical phenomena that comes before the half reaction such as homogeneous or heterogeneous chemical equilibria.

The mass transport rate is the factor that most voltammetric techniques seek to control. Such systems are called *nernstian* or *reversible*, because they obey thermodynamic relationships (Kolliopoulos, 2014). The transport of species to the electrode surface in addition to the electrode reaction can occur by any of the following processes.

- Diffusion – Transport of species due to concentration gradient.
- Convection – Transport due to mechanical motion of the solution as a result of stirring.
- Migration – Transport of ions due to the electrostatic attraction between the oppositely charged electrode and the ions.

In all the dynamic electroanalytical methods, conditions are created in the solutions so that the migration of the electroactive species can be neglected. This is achieved by the addition of a large excess of an inert electrolyte called the supporting electrolyte. If the solution is kept unstirred convection can also be eliminated, leaving the transport process to take place by diffusion alone. The current then achieved is called diffusion controlled limiting current (Isaac, 2011).

2.7 Sensors

A sensor can be defined as device which senses a particular analyte or a substance. It is a device which measures a physical quantity and converts it into a signal which can be read by an instrument. Sensors are designed to detect and respond to an analyte in the gaseous, liquid or solid state (Isaac, 2011). The purpose of a (chemical) sensor is to provide real-time reliable information about the chemical composition of its surrounding environment. Ideally, such a device is capable of responding continuously and reversibly and does not perturb the sample. Such devices consist of a transduction element covered with a chemical recognition layer (Wang, 1995). The role of these two important components in sensors is to transmit the signal from a selective compound or from a change in a reaction. These devices produce signals such as electrical, thermal or optical

output signals, which are converted into digital signals for further processing. The most important aspects of sensors are sensitivity, selectivity, and stability (Oluoch, 2016).

Sensors can be broadly classified into physical and chemical sensors. Physical sensors are sensitive to such physical responses as temperature, pressure, magnetic field, force and do not have a chemical interface.

Chemical sensors rely on particular chemical reactions for their response (Isaac, 2011). They respond to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative and quantitative determination of the analyte. The role of the chemical sensor is to provide information about the chemical state of the process and one can assume that the chemical sensor is the “eye” of the process control system. There are two parts to a chemical sensor: a region where selective chemistry takes place and the transducer (Isaac, 2011). Chemical sensors can be classified into the following depending on the transducer types:

- i. Optical sensor
- ii. Mass sensitive sensor
- iii. Heat sensitive sensor
- iv. Electrochemical sensor

Electrochemical sensors have several advantages over the other sensors (optical, mass sensitive and heat sensitive) because they can sense the materials which are present within the host without doing any damage to the host system. They have high degree of selectivity and sensitivity, remarkable detectability, experimental simplicity, low cost and reproducibility. They are frequently used in clinical diagnostics, occupational safety, medical engineering, process measuring engineering, and environmental analysis. They are widely used in the determination of concentrations of various analytes in samples such as fluids and dissolved solid materials. (Isaac, 2011; Oluoch, 2016).

2.7.1 Electrochemical sensors

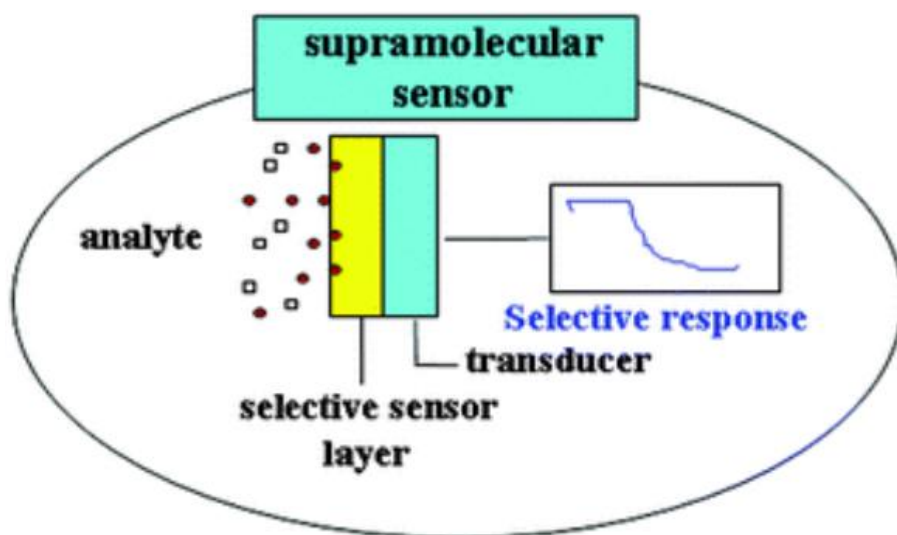
In the case of electrochemical sensors, the analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer (Wang, 1995). There are three major types of electrochemical sensors which include voltammetric, potentiometric and amperometric sensors (Zohreh, 2016).

In voltammetry, the current and the potential are measured and recorded. The position of peak current is related to the specific chemical and the peak current density is proportional to the concentration of the corresponding species. Low noise and simultaneous detection of multiple analytes are the advantages of this technique (Zohreh, 2016).

The Potentiometric sensor interface has a local equilibrium where either the membrane or electrode potential is measured, and information about the composition of a sample is obtained from the potential difference between two electrodes. In this technique, a gas-sensing electrode or an ion-selective electrode is the transducer (Zohreh, 2016).

Amperometric sensors are based on the detection of electroactive species involved in the chemical or biological recognition process. The signal transduction process is accomplished by controlling the potential of the working electrode at a fixed value (relative to a reference electrode) and monitoring the current as a function of time. The applied potential serves as the driving force for the electron transfer reaction of the electroactive species. The resulting current is a direct measure of the rate of the electron transfer reaction. It is thus reflecting the rate of the recognition event, and is proportional to the concentration of the target analyte (Wang, 1995).

Electrochemical, particularly voltammetric sensors are fabricated in the present investigation. Among the various potentiodynamic voltammetric techniques, cyclic voltammetry and difference pulse voltammetry are employed in the present work.



Scheme 2. 1 Series of recognition process typical in sensors (Oluoch, 2016)

2.8 Electrodes

An electrode or electrode materials can be defined as a substance whose surface serves as the channel where oxidation-reduction equilibrium is established between the metal and what is in the solution (analyte). There are two type or electrodes, either cathode or anode. An anode receives the currents or electrons from the electrolyte mixture, thus oxidizing the electroactive species in the solution, when the atoms or molecules get close enough to the surface of the electrode; the electroactive species solution in which the electrode is placed into donates electrons. This causes the atoms/molecules to become positive ions. Examples of electrodes are platinum (Pt), gold (Au), Palladium (Pd), Carbon, or a semi-conductor such as (SnO_2). The electrode composition must have some interesting electrode properties such as electrical conductivity, chemical stability, surface reproducibility, mechanical properties, availability and lower toxicity. The working electrode determines the electrochemical performance of voltammetric experiment based on the fact that the targeted electrochemical changes occur on the working electrode (Olayiwola, 2016).

A good working electrode must have high signal to noise ratio and good reproducibility. The electrochemical interpretation of this statement is that before an electrode is chosen for electrochemical experiment, it must have features such as high surface area, electrochemical

conductivity, redox behavior of the target analyte, back ground current over the potential region required; it must be affordable and have reproducibility features. There are many types of electrodes, some of them will be discussed briefly (Olayiwola, 2016).

2.8.1 Mercury electrodes

There are different types of mercury electrodes which are dropping mercury electrode, hanging drop electrode and mercury film electrode. Among these types of Hg electrodes, dropping mercury electrode is the most commonly used. The advantage of using a mercury electrode is that the electrode can be self-renewing which means that it does not need to be cleaned or polished before each experiment like exfoliated graphite and glassy carbon electrodes. More so, each drop of mercury has an uncontaminated and uniform surface. Unfortunately, despite these promising advantages of dropping Hg electrode, it had been restricted for usage because of the gravity of its toxicity which is mercury poisoning and the limited anodic range in the analysis for biological species (Olayiwola, 2016).

2.8.2 Gold electrodes

A Gold electrode has superior qualities to all other types of electrodes; it has been used for wide applications in electrochemistry. The value of Au nanoparticles is that it can be used in its nano-form to modify the surface of an electrode and can also be used as an electrode. The short coming of using an Au electrode is that they are expensive and when used to modify an electrode they tend to be obstinate or difficult to remove from the electrode surface (Olayiwola, 2016).

2.8.3 Carbon electrodes

Carbon is the most widely utilized electrode material in electroanalytical chemistry and it is available in a large variety of structures: graphite, glassy carbon (GC), amorphous carbon, diamond, carbon nanotube and carbon fiber, each with different electrochemical properties (Kolliopoulos, 2014). Carbon electrodes have been extensively used as an electrode substrate to make various electrodes. The soft properties of carbon makes these electrode surfaces easily renewable for electron exchange. The outstanding properties of carbon electrodes over all other

electrodes are: broad potential window, low background current, rich surface chemistry, comparative chemical inertness, easy modification, great versatility and low cost. The most prevalent carbon electrodes used are pyrolytic graphite electrode (PGE), glassy carbon electrode (GCE), carbon paste electrode, carbon fibre electrode and electrodes composed of carbon composite. Glassy carbon electrode (GCE) is the most widely used electrode of all carbon based electrodes (Olayiwola, 2016).

2.8.3.1 Glassy carbon electrode (GCE)

In this study, GCE was utilized because it possess the properties of both glassy and ceramic materials combined with graphite. The application of GCE as a WE for voltammetry was proposed initially by Zittel and Miller, (1963). Its specific surface orientation, extreme resistance to chemical attack and impermeability to gases and liquids renders them suitable as an electrode material for sensor fabrication. The advantage of GCE over other electrodes is that they can operate in positive as well as negative potentials (Theresa, 2015).

2.9 Electrochemical sensing

There are several publications in which modified glassy carbon electrodes have been explored for the detection of arsenic (III) (Shin and Hong, 2010; Idris et al., 2017; Karthika et al., 2019), 2-chlorophenol (Dong and Huajie, 2006; Maochao Wei et al., 2014; Zhu et al., 2018) and sulfamethoxazole (Zhang, 2020; Khanfar et al., 2020) using CV or DPV. In most cases, the detection limits were found to be close or lower than the WHO standards (Abdollah Salimi et al., 2008; Xiao et al., 2008; Lia et al., 2013; Fernández et al., 2013; Salmanpour, 2019).

2.9.1 Electrochemical detection of 2-chlorophenol

2-chlorophenol is electroactive and has been determined using techniques such as square wave voltammetry, DPV and CV. Lia et al., (2013) explored a nanocomposite of cetyltrimethylammonium bromide (CTAB) and ZnSe quantum dots to modify the surface of

glassy carbon electrode for the detection of chlorophenols. DPV was used for the quantitative determination of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) at a pH of 6. The detection limits were 0.008, 0.002 and 0.01 μM , respectively. The method was successfully applied for the determination of CPs in waste water with satisfactory recoveries. The ZnSe–CTAB/GCE electrode system provides operational access to design environment-friendly chlorophenol sensors.

Dong et al. (2006) investigated the use of acetylene black (AB) and dihexadecyl hydrogen phosphate (DHP) as a modifier of a glassy carbon electrode surface for 2-chlorophenol detection. The response to 2-chlorophenol on the modified electrode was examined using DPV at pH 7. The results showed that the AB-DHP film-modified GCE significantly enhanced the oxidation peak current of 2-chlorophenol, and thus greatly improved its determining sensitivity. The detection limit was found to be 0.05 μM .

Li (2006) constructed multi-wall carbon nanotubes with dicetyl phosphate (MWNT-DCP) composite film coated on glassy carbon electrode for 2-chlorophenol sensing in water. The MWNT/DCP/GCE electrode significantly enhanced the oxidation peak current of 2-chlorophenol when detected, using DPV at pH of 6. The oxidation peak current increased linearly with the concentration in the range of 0.1 – 20 μM and the detection limit was found to be 0.04 μM .

Shi and Zhu (2011) fabricated a novel electrochemical sensor for 2-chlorophenol using the Pd-graphene nanocomposite and ions liquid (IL-Pd-graphene). The electrocatalytic properties were investigated by CV and DPV at pH of 7.4. It indicated that the IL/Pd/grapheme/GCE nanocomposite had a high activity for 2-chlorophenol oxidation. The achieved detection limit was 1.5 μM .

Horseradish peroxidase (HRP) was immobilized on a film of Co–Al layered double hydroxide or hydrotalcite-like clay (HT), modified with sodium dodecylbenzenesulfonate (SDBS) and casted on a glassy carbon electrode GCE for the detection of 2-chlorophenol. The HRP-SDBS-HT-GC modified electrode was successfully employed for the detection of 2-chlorophenol using CV. The

linear range was from 0.005 to 0.05 μM with a detection limit of 0.002 μM (Fernández et al., 2013).

In another study, Zhu et al. (2018) employed a novel electrode based on functionalized carbon nanotubes and rhodamine B (f-CNTs/RhB) to monitor the concentration and toxicity of 2-chlorophenol. The peak current of 2-CP was enhanced on the f-CNTs/RhB/GCE electrode and was linear with concentrations ranging from 0.05 to 125.0 μM and the detection limit was 0.028 mM under optimal testing conditions (pH 3).

Wei et al. (2014) were able to detect trace amounts of 2-chlorophenol on a carbon paste electrode modified with β -cyclodextrin (CD) functionalized grapheme. The electrochemical behaviour of 2-CP on the CD/GRs/CPE electrode was investigated by (CV) and (DPV). The results demonstrated that the CD/GRs/CPE exhibited enhanced sensitivity towards 2-chlorophenol detection with a detection limits of 0.2 μM .

2.9.2 Electrochemical detection of Arsenic (III)

Inorganic arsenic can be electrochemically oxidized or reduced and thus can be electrochemically detected. Arsenic (III) can be directly oxidized to As (V) on an electrode surface under the application of an appropriate potential, and thus the analyte concentration can be determined by recording its oxidization current. In addition, As (III) can also be reduced to As (0) electrochemically, and thus the level of inorganic arsenite can also be detected by measuring the reduction current (Xu et al., 2020).

For the voltammetry analysis of inorganic As (III), two steps are involved in sequence. The first step is the pre-concentration or deposition of As(III) at the cathode. The As (III) species is electrochemically reduced to As (0) and enriched onto electrode surfaces under an appropriate constant potential. The second step is the stripping of the enriched As (0) at the anode. With the drive of a positive-going potential, the As (0) species is oxidized to As(III) again, giving the stripping signal for the quantification of As (III) (Xu et al., 2020). The electrochemical detection of arsenic can be represented as the following equations:

Deposition: $\text{As}^{3+}(\text{aq}) + 3\text{e}^{-}(\text{m}) \rightarrow \text{As}(\text{m})$Equation 2.1

Stripping: $\text{As}(\text{m}) \rightarrow \text{As}^{3+}(\text{aq}) + 3\text{e}^{-}(\text{m})$Equation 2.2

Arsenic (III) was detected with square wave anodic stripping voltammetry by Yanga et al. (2016) using bimetallic gold-copper nanoparticles with different compositions of Au-Cu on a glassy carbon electrode. The Au-Cu bimetallic nanoparticles showed enhanced electrochemical performance with high sensitivity at ppb level and low detection limit. Moreover, the $\text{Au}_{89}\text{Cu}_{11}$ bimetallic nanoparticles exhibited ultra-high and anti-interference performance for the detection of arsenic (III). The limit of detection were found to be 5.64 ppb, 3.43 ppb, 2.09 ppb and 12.8 ppb on Au, $\text{Au}_{93}\text{Cu}_7$, $\text{Au}_{89}\text{Cu}_{11}$ and $\text{Au}_{79}\text{Cu}_{11}$ bimetallic nanoparticles modified electrode, respectively.

Salimi et al. (2008) investigated the use of cobalt oxide nanoparticles on a glassy carbon electrode surface for arsenic (III) detection. The response to As^{3+} on the modified electrode was examined using cyclic voltammetry and the detection limit was 11 nM and sensitivity of 111.3 nA/ μM . Nano Au-crystal violet (CRV) film was fabricated and used to modify a glassy carbon electrode for the detection of arsenic (III) in various water samples using cyclic voltammetry (Rajkumar et al., 2011). The nano Au-CRV film modified GCE successfully detected the arsenic in the linear range of 4-40 μM with the detection limit of 0.20 μM .

Gold nanoparticles were deposited on multiwalled carbon nanotubes (CNTs) and the resulting gold covered nanotubes (Au/CNTs) were immobilized onto the surface of a glassy carbon electrode and used for the detection of arsenic (III) via anodic stripping voltammetry (Xiao et al., 2008). A limit of detection of 0.1 g/L was obtained in that study.

Toor et al. (2015) assessed the electrochemical detection of trace amount of arsenic (III) with a low detection limit by CV on a glassy carbon electrode modified with Au/ Fe_3O_4 nanocomposite. The results showed that the synthesized nanocomposite had very good potential towards As (III) detection and can be optimized further for low level detection of it.

The modification of the GCE with gold nanoparticles (AuNPs) was developed and used for the detection of arsenic (III); the modified electrode showed an increased oxidation current of arsenic (III) (Idris et al., 2017). The detection was carried out using square wave anodic stripping voltammetry at pH 1. The GCE/AuNPs electrode detected As(III) to the limit of 0.28 ppb.

The electrochemical detection of As (III) was investigated by Shin and Hong (2010) on a platinum-iron (III) nanoparticles modified multiwalled carbon nanotube on a glassy carbon electrode (nanoPt-Fe (III)/MWCNT/GCE). The resulting electrode was examined by cyclic voltammetry (CV), and anodic stripping voltammetry (ASV). For the detection of As(III), the nanoPt-Fe(III)/MWCNT/GCE showed a low detection limit of 10 nM (0.75 ppb) and a high sensitivity of $4.76 \mu\text{A}\mu\text{M}^{-1}$. The WHO's guideline value of arsenic for drinking water is 10 ppb.

An electroreduced graphene oxide (ERGO) and Au nanoparticles (AuNPs) composite film was electrodeposited on a glassy carbon electrode by cyclic voltammetry (Liu et al., 2013). The fabricated ERGO-AuNPs/GCE was used to determine As (III) by anodic stripping voltammetry (ASV) and the detection limit was 2.7 nM (0.20 ppb).

Strontiumtitaniumtrioxide (SrTiO_3) decorated β -cyclodextrin (β -CD) nanocomposite modified glassy carbon electrode was developed for the efficient and accurate determination of poisonous arsenic (III) ions in water and blood serum samples (Karthika et al., 2019). The synthesized SrTiO_3/β -CD nanocomposite showed a sensitive electrochemical response for the oxidation of arsenic (III). The oxidation peak current of arsenic (III) was obtained by amperometric and under the optimized conditions, the detection limit was found to be 0.02 μM .

2.9.3 Electrochemical detection of sulfamethoxazole (SMX)

Due to its fast response and low cost of electrochemical analysis, electrochemical sensors have found more popularity compared to the other analytical techniques for drug analysis in recent years. Although the electrochemical sensors are of choice for detection of drugs, the overvoltage and weak oxidation current of sulfamethoxazole are the main problems for determination of this

drug at low level concentrations. To overcome these problems, modified sensors are appropriate choices given their high conductivity and low charge transfer resistance (Salmanpour, 2019). One of the electrochemical property of sulfamethoxazole is that it undergoes an irreversible oxidation reaction as shown in **Figure 2.4**. The generated oxidation current is directly proportional to the oxidized species concentration (Khanfar et al., 2020).

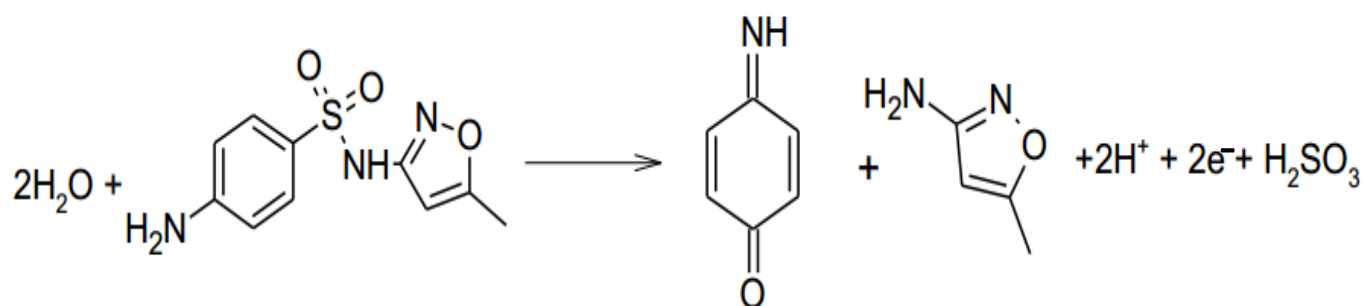


Figure 2. 4 Electrochemical oxidation reaction of sulfamethoxazole (Khanfar et al., 2020)

Although various electrode modifying materials have been widely used in electrochemical research for SMX detection in water samples as well as human serum on diverse electrodes, the detection of SMX on GCE modified with g-C₃N₄/CDs has not been reported.

An Ag₂O/MWCNTs nanocomposite material was prepared and used to modify a glassy carbon electrode for sulfamethoxazole detection (Zhang, 2020). The obtained Ag₂O/MWCNTs/GCE electrode exhibited good electrochemical performances with a pair of quasi-reversible redox peaks. SMX interacted with Ag (I) to form Ag-SMX complex, which decreased the concentration of silver ion involved in the redox reaction, thus reducing the redox peak of the Ag₂O/MWCNTs composites. The decreased oxidation peak current was found to be linear with the SMX concentrations from 0.02–100 nM and the detection limit was 4.06×10^{-12} M by using the DPV technique. Furthermore, the proposed method demonstrated excellent selectivity, repeatability and reproducibility and was successfully applied for the SMX analysis in human serum.

Glassy carbon electrodes were modified by molybdenum and manganese oxides (MoO₂ and MnO₂) and used as catalysts for the electrochemical oxidation of sulfamethoxazole (SMX) (Khanfar et al., 2020). The analytical performance of the modified electrodes was evaluated based

on the following statistical parameters; linearity ranges, correlation coefficients, limits of detection and quantitation, and recovery values. The prepared electrode was used for the determination of SMX with DPV in its pharmaceutical formulations and the reported limit of detection was found to be 0.144 μM with a range of 10-100 μM .

A molecularly imprinted (MIP/GCE) electrochemical sensor for the detection of sulfamethoxazole was prepared by electro polymerization with sulfamethoxazole as template molecule and o-phenylenediamine as functional monomer (Zhang, 2019). The electrochemical performance of molecularly imprinted sensor was studied by cyclic voltammetry in 0.1 M KCl solution containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$. Under optimal experimental conditions, square wave voltammetry was used to detect sulfamethoxazole. The square wave voltammetric peak current difference of the sensor had a good linear relationship with the concentration of sulfamethoxazole in the range from 0.2 to 1.4 μM and the detection limit was 0.05 μM . The molecularly imprinted sensor had good selectivity, repeatability and stability when used for water sample analysis.

The detection of sulfamethoxazole was performed at a multiwalled carbon nanotube (MWCNT)-Nafion modified glassy carbon electrode (GCE) (Issac and Kumar, 2009). The amount of MWCNT-Nafion suspension, the pH of the supporting electrolyte and scan rate were optimized and a direct electrochemical method for the determination of SMX was developed. Under optimum conditions (pH 8), the oxidation peak current appeared at 0.74 V and was linear to the concentration of SMX in the range $1 \times 10^{-2} - 5 \times 10^{-5}$ M with a detection limit of 1×10^{-5} M. The MWCNT/Nafion/GCE showed good stability, selectivity and was successfully used to quantify SMX in pharmaceutical formulations and urine samples.

A glassy carbon electrode (GCE) modified with a nanocomposite prepared from graphitic carbon nitride and zinc oxide (g- $\text{C}_3\text{N}_4/\text{ZnO}$) was developed for the determination of sulfamethoxazole (Balasubramanian et al., 2018). Under the optimal conditions, the response of the electrode, typically measured between 0.8 and 0.9 V, increased linearly with the concentration of SMX from 20 nM to 1.1 mM range and a detection limit of 6.6 nM was obtained. The modified electrode was highly selective, well reproducible and maintained its activity for at least 4 weeks.

Yue et al. (2020) developed a novel electrochemical sensor based on graphene (GR) and ZnO nanorods (GR-ZnO/GCE) to detect sulfamethoxazole (SMX). The electrochemical experiment results showed that the synergetic effect of GR and ZnO gave the prepared sensor excellent

electrocatalytic behavior towards the oxidation of SMX. SMX was detected by DPV method at 0.85 V. Under the optimal conditions, the GR-ZnO/GCE showed superior wide linear responses in a concentration range of 1–220 μM for SMX with the limit of detection (LOD) of 0.4 μM . In addition, the sensor had good stability, good selectivity, anti-jamming ability and reproducibility. The electrochemical detection was also tested in lake water, tap water, urine and serum with recovery between 93.2% and 108%. The proposed sensor provided a good application prospects in biomedicine and environmental protection.

The results obtained from these studies suggested that glassy carbon electrodes are efficient, and reliable for electrochemical studies. The excellent reports obtained from the literature for GCE activated our interest in utilizing it for this study. It is important to modify glassy carbon electrode so as to enhance the electrocatalytic and electrochemical properties of its surface. The chemistry of the electrochemical modification of electrode will be discussed next in this work.

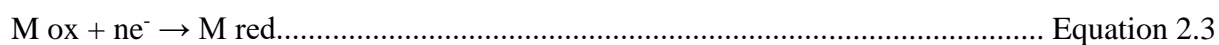
2.10 Electrodes modification

Chemical layers can also be used for imparting a high degree of selectivity to electrochemical transducers. Powerful sensing devices can be designed by a deliberate modification of their surfaces. Basically, the modification of an electrode involves immobilization on its surface of reagents that change the electrochemical characteristics of the bare surface. Such manipulation of the molecular composition of the electrode thus allows one to adjust the response to meet specific sensing needs. Electro catalysis involves an electron transfer mediation between the target analyte and the surface by an immobilized catalyst. Such catalytic action results in faster electrode reactions at lower operating potentials (Wang, 1995). Various materials have been utilized to modify electrodes and have been successfully employed for facilitating the detection of water pollutants, i.e., metal nanoparticles, metal oxides, metal sulfides, metal-organic frameworks, and carbon materials (He et al., 2018).

2.10.1 Chemical modified electrodes (CMEs)

An active area of research in electrochemistry is the development of new electrodes produced by chemically modifying their surface with various conductive substrates. Such electrodes have been tailored to accomplish a broad range of functions. Modifications include applying irreversibly adsorbing substances with desired functionalities, covalent bonding of components to the surface and coating the working electrode with films made from polymer or other substances. One of the most important properties of CMEs is their ability to catalyze the oxidation or reduction of solute species that exhibits high voltages at unmodified surfaces. Thus CMEs play an important role in reducing the high overvoltage required for the voltammetric determination of an analyte without its major interferences (Isaac, 2011).

The chemistry of the reaction between the bare electrode and the modifier is that the redox active sites shuttle electrons between the analyte and the electrodes with significant reduction in activation potential. Redox reactions on the surface of the electrode can be enhanced and explored by using a suitable electron transfer mediator. The promising advantage of the mediator is to expedite the charge transfer between the electrode and the analyte. The chemical reactions between the electrode and the analyte can be represented as follows, where M represents the mediator and A is the analyte:



The importance of mediator-modified electrode is that it can reduce the over potential of the analyte and the possibility of interfering background current. In addition to this, the response of the current signal can also be enhanced and lowering of the detection limit can be achieved. The challenge of modifying an electrode is that it is difficult to maintain long term stability. Unfortunately, the electrochemical activity of modified electrodes gradually decreases due to the detachment and dissolution of the catalyst from the substrate. To overcome the difficulties of electrode modification challenges an electrode with high sensitivity and long term stability has to

be generated; a simple method such as the sol-gel technique can be used for preparing a modified electrode (Olayiwola, 2016).

Various substrates such as Carbon Nanotubes (CNT), Gold nanoparticles (AuNPs), Polymer films, and carbon Nanoparticles (CNPs) are used for the modification of electrode surface (Isaac, 2011). For the present study, the modification techniques adopted are CNPs based because of their outstanding properties.

2.10.2 Carbon nanoparticles (CNPs)

Carbon, as one of the most versatile elements in the earth, has attracted a great deal of attention especially due to its ability to form different types of hybridization states (sp , sp^2 and sp^3) that makes it capable of forming a wide range of allotropes from diamond which is the hardest material ever discovered to graphite as the softest one (Asadian et al., 2019). With the emergence of nanotechnology, carbon nanostructures have been the subject of intense investigations.

With the emergence of nanotechnology, carbon-based nanomaterials such as carbon nanotubes (CNTs), carbon nanoparticles (CNPs) and graphene have been synthesized and broadly investigated due to their superior electronic, physical, optical and magnetic properties. Recently, researchers have focused on carbon nanoparticles (CNPs) as a highly attractive carbon nanomaterials, due to their properties such as small size (typically < 10 nm), ease of preparation within a wide range of synthesis methods and precursors, nontoxicity and good biocompatibility, excellent chemical stability as well as high solubility in both polar and nonpolar solvents owing to the presence of various functional groups on their surface (Asadian et al., 2019).

Furthermore, CNPs have shown tremendous potential for electrochemical sensing due to offering numerous advantages like intrinsic electrochemical activity, large specific surface area, electrocatalytic properties, facilitated electron transfer and outstanding electrical conductivity. CNPs are good candidates for surface functionalization due to numerous reactive surface sites, which allow the surface functionalized CNPs to be adsorbed onto the electrode surface via electrostatic interactions. CNPs not only leads to a highly porous structure with enlarged specific

surface area, but also increases the electrical conductivity of the final composite electrode. CNPs, when used as modifiers, can enhance the electron transfer kinetics along with overpotential reduction, but also improve the sensitivity through increasing the peak current as well (Alim et al., 2018).

2.10.2.1 Graphitic carbon nitride (g-C₃N₄)

Graphitic carbon nitride (g-C₃N₄) is an attractive carbon semiconductor material which possesses a graphite-like structure; g-C₃N₄ was discovered in the 1830s (Zhao et al., 2017). Graphitic carbon nitride is an analogue of graphene; it has been of great interest due to the strong electron donor nature of nitrogen present in its structure (Lee et al., 2017). Graphitic carbon nitride is composed of carbon and nitrogen atoms with layered structure similar to graphite (**Figure 2.5**). Bonding in g-C₃N₄ is dominated by sp²-bonded carbon and nitrogen atoms and like graphene and there are many free π electrons within the layer (Wang et al., 2013). It is the most stable structure of all carbon nitrides at room temperature and it has a layered structure involving weak van der Waals interaction (Mert et al., 2018). The formed tris-s-triazine is connected to each other via a tertiary amine which gives it high and stable thermal and chemical properties (Zhang et al., 2018). The presence of nitrogen increases its characteristics of electron donor/acceptor (Rana et al., 2020).

Even though g-C₃N₄ possesses similar N atoms to pyridine-like nitrogen, the potential electrochemical catalytic property of g-C₃N₄ is greatly depressed by the poor conductivity and low surface area. Therefore, the application of g-C₃N₄ in electrochemical sensing is still challenging and rarely reported (Xu et al., 2018). Much effort has been devoted to solving such problems that hamper the applications of g-C₃N₄ in the field of electrochemical sensing (Zhang et al., 2018). Aiming to enhance the electrochemical sensing of g-C₃N₄, several strategies, mainly doping, coupling with other semiconductors or modification with other carbon materials have been attempted (Zhang et al., 2018).

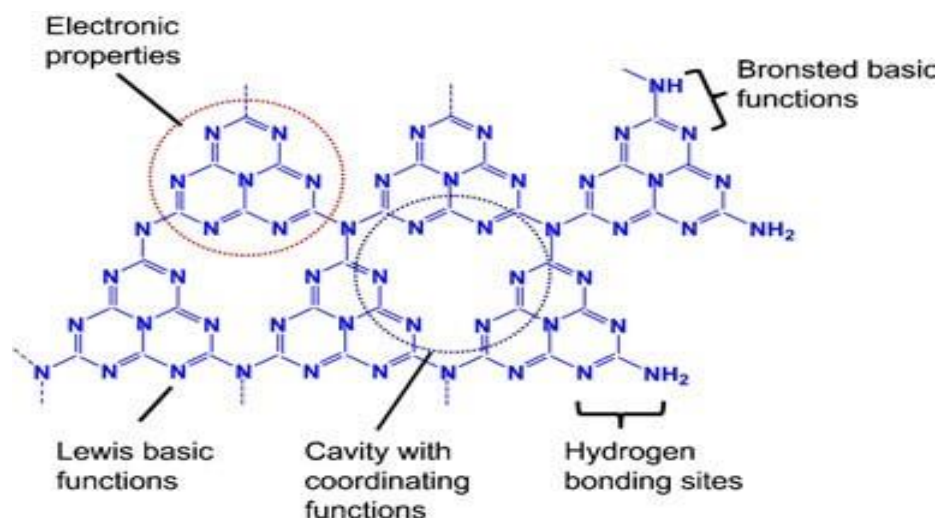


Figure 2. 5 Single layer structure of graphitic carbon nitride based on tri-s-triazine (Wang et al., 2013)

2.10.2.1.1 Graphitic carbon nitride as electrode modifier

Ahmad et al. (2020) reported on the preparation of fluorescent oxygen and sulfur co-doped g-C₃N₄ quantum dots and utilized them for Cu²⁺ detection. They obtained enhanced sensing toward Cu²⁺ due to better dispersion, stability of g-C₃N₄ quantum dots in water, and improved optical properties.

Wang et al. (2013) used graphitic carbon nitride modified with a bismuth film as an electrode modifier for the detection of lead (II) using differential pulse anodic stripping voltammetry (DPASV). The combination of such materials has shown great improvement in the sensing capability of the electrode. The properties of g-C₃N₄ was advantageous in the detection process because of its structure (tri-s-triazine) which is the most stable among many. The g-C₃N₄/Bi electrode demonstrated a high current response superior to the other electrodes confirming that g-C₃N₄ was a useful material to detect Pb²⁺. The g-C₃N₄ electrode showed rapid electron transfer because g-C₃N₄ is dominated by sp²-bonded carbon and nitrogen atoms with abundant π electrons in the layers. It can efficiently attract trace metal ions commendably by electrostatic attraction

forces. Secondly, Pb^{2+} was able to coordinate with several N-atoms of g- C_3N_4 or enters into the layers of g- C_3N_4 during accumulation. The detection limit was found to be 2.0 pM.

Zhao et al. (2017) used graphitic carbon nitride to enhance the electrochemical response of tetrabromobisphenol-A (TBBPA) at glassy carbon electrode. TBBPA was quantified with the modified electrode in the range of 0.02 μM - 1 μM with a detection limit of 5 nM using CV and DPV. The properties of the modified electrode also enabled its application in environmental samples detection. Compared to the pyridine-like nitrogen, which could donate one electron to the carbon ring, the graphite-like nitrogen with sp^2 hybridization might donate two electrons and provide more electrochemical active sites to improve the electrochemical activity of the materials (Zhao et al., 2017).

Xu et al. (2018) developed a fast, ultrasensitive electrochemical sensing platform based on graphitic carbon nitride and electrochemically deposited-poly(3,4-ethylenedioxythiophene) (g- C_3N_4 -E-PEDOT) composite by *in-situ* electro-polymerization. It was applied for the quantitative determination of acetaminophen (AP). E-PEDOT was introduced as the conducting matrix for developing the composite to complement the poor conductivity of g- C_3N_4 . The strong affinity and synergetic effect between g- C_3N_4 and E-PEDOT highly improved the electron transfer property and enhanced the electrochemical catalytic activity of the composite. The g- C_3N_4 /E-PEDOT modified glassy carbon electrode (GCE) demonstrated better electrocatalytic activity towards the oxidation of AP than unmodified g- C_3N_4 and E-PEDOT. An ultra-low limit of detection of 34.28 nM was obtained. The excellent sensing performance of g- C_3N_4 /E-PEDOT can be attributed to the high conductivity and good electrocatalysis of E-PEDOT as well as the catalytic pyridine-like nitrogen atoms of g- C_3N_4 . Simultaneously, the good combination and the π -conjugation of g- C_3N_4 with E-PEDOT also played important roles and enabled the fast electron transfer inside the g- C_3N_4 -E/PEDOT composite. It also exhibited significant synergistic effects.

2.10.2.2 Carbon dots (CDs)

Carbon nanoparticles were accidentally discovered by Xu et al. (2004) during the electrophoretic purification of single-walled carbon nanotubes (SWCNTs). Sun et al. (2017) reported the synthesis

of fluorescent carbon particles of size less than 10 nm and which they called “carbon dots”. Carbon-dots (CDs) have an unprecedented and remarkable properties including multicolor wavelength tuned emission, up-conversion photoluminescence, high quantum yield, aqueous dispersibility, high biocompatibility, low toxicity, great aqueous stability, facile synthesis, high photo stability, chemical inertness, greater surface areas, greater surface active sites, fast electron transfer, electron reservoir and supernal conductivity features.

CDs primarily consist of C, H, N and O elements (**Figure 2.6**) which are present in the form of various functional groups and provide good water solubility with scope for further functionalization (Sharma et al., 2017). Hydroxyl, carbonyl and amino functional groups on its surface can mediate solubility in the aqueous solutions and enhance the catalytic actions of the original substances (Tajik et al., 2020).

Their internal carbon linkage by sp^2 confers the chemical ability to be converted in smallest units (Algarra et al., 2018). The nano-scaled size of CDs leads to the quantum-confinement effect which results in interesting optical and electronic properties such as high quantum yield (Liu et al., 2007). Due to the enclosure and edge effects of quantum, the CDs have higher speed electron transfers and conductivity. CDs can also catalyze the redox reaction (Tajik et al., 2020).

Carbon dots are generally quasi-spherical nanoparticles comprising amorphous to nanocrystalline and always consist of sp^2/sp^3 carbon, oxygen/nitrogen based groups, and post-modified chemical groups (Sun and Lei, 2017). In electrochemical sensors, carbon dots employed as electrode material, can accelerate charge transport and redox reactions, enhance selectivity, conductivity, stability, and reproducibility of sensors. So, they are considered as indispensable components of high performing electrochemical sensors. Their large surface area enables them to immobilize molecules by simple adsorption or other techniques. In addition, various functional groups on their surface CDs facilitate the attachment of biomolecules (Dinç and Günhan, 2019).

By taking into account all the above considerations, CDs can increase the precision and accuracy of bio and chemical sensors (Dinç and Günhan, 2019). Hence, due to these outstanding properties, utilizing carbon dots as modifiers on a bare electrode for electrochemical sensing has been considered as an encouraging option. Due to the unique properties of carbon dots, they could serve

as sensors for a broad range of analytes, such as ions, small molecules, macromolecules, cells and bacteria (Sun and Lei, 2017).

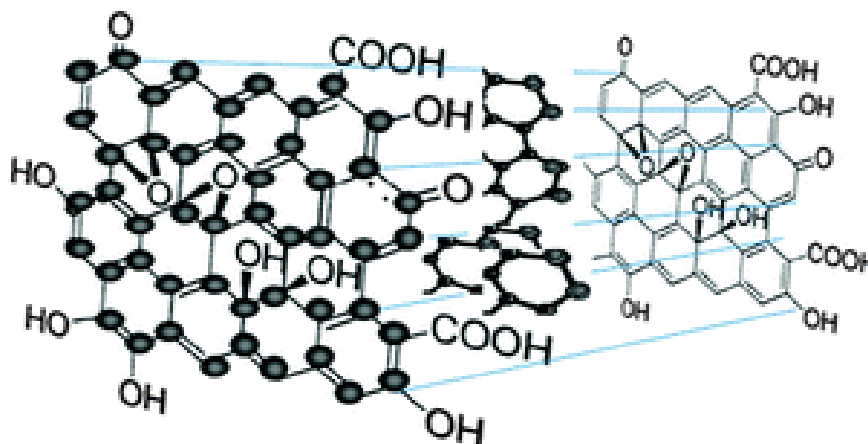


Figure 2. 6 Chemical structure of CDs (Lim et al., 2015)

In the following sections, carbon dots based sensing of different analytes is presented:

2.10.2.2.1 Carbon dots as an electrode modifier

Algarra et al., (2018) developed a glassy carbon electrode (GCE) whose surface was modified with carbon quantum dots CDs. It was applied for the effective enhancement of the electrochemical signal for dopamine and uric acid determination using CV. The modified GCE (CDs/GCE) exhibited a sensitivity that was almost 10 times better than of the original (GCE). The lower limits of detection were 1.3 μM for uric acid and 2.7 μM for dopamine. The synthesized CDs have proven to enhance the response towards uric acid and dopamine determination.

CDs modified nanocomposites can play a crucial role in lowering the resistance charge transfer and oxidation potential of an electrode. Due to its great specific surface area, CDs can also increase the electron transfer rate on the electrode surface. CDs have been reported to lower the electron

transfer resistance and to increase the electrical conductivity of nitrogen-doped carbon dots (N-CDs/Cu₂O/GCE) decorated copper oxide electrodes for the determination of the non-steroidal anti-inflammatory drug aspirin (ASA) in berries using DPV (Muthusankar et al., 2018). The limit of detection was found to be 0.002 μ M, with a linear range of 1–907 μ M. The developed sensor displayed outstanding repeatability, stability and accumulation time along with better electrocatalytic response for real-life application.

CDs has been reported to improve the effective electroactive surface area and electron transportation. Zhenga et al. (2018) proposed for the first time a novel molecularly imprinted electrochemical sensor (MIECS) based on a glassy carbon electrode (GCE) modified with carbon dots and chitosan (CS) for the determination of glucose via differential pulse voltammetry. The use of the environmental-friendly CDs and CS as electrode modifiers (CDs-CS/GCE) improved the active area and electron-transport ability substantially. The limit of detection was found to be 0.09 μ M (S/N=3). The redox peak current significantly increased due to the surface structure of CDs which stimulated the electron transfer rate of the redox system.

CDs can create a highly porous modifier layer which led to a significant enhancement of the surface area and provide adsorption sites on the modified electrode surface which not only cause a remarkable enhancement in the peak currents, but also facilitate its sensitive analysis with lower detection limit (Asadian et al., 2019). Hence, the efficiency of most of the CDs modified electrodes is partially due to the high adsorption ability of CDs towards various analytes (Asadian et al., 2019).

The adsorption process of drug compounds and organic molecules on CDs can be realized through π – π interactions. Charged analytes can effectively adsorb functional groups on their surface with the aid of electrostatic interactions (Asadian et al., 2019). The detection of heavy metals in water samples has attracted a great deal of attention among researchers during the past few decades. Fortunately, heavy metals are electroactive and can undergo redox reactions. They can be detected by electrochemical methods based on the change in the current, potential, capacitance or impedance (Asadian et al., 2019).

Zimer et al. (2003) were the first to prepare an electrochemical sensor by drop casting a CDs/polyaniline composite suspension at the surface of an Indium Tin oxide electrode and used it for determination of Cu^{2+} and Pb^{2+} ions by anodic stripping voltammetry. The modified electrode (PANI-CDs) exhibited better physical stability and a higher analytical response to the target ions at ppb concentration levels. A detection limit of 0.85 and 1.61 ppb was obtained for Cu^{2+} and Pb^{2+} , respectively (Zimer, 2003).

Shao et al. (2013) designed a highly selective sensing platform for electrochemical monitoring of cerebral Cu^{2+} ions. The electrode was modified with CDs, possessing high active surface area and unique electrocatalytic activity. The prepared sensor exhibited high selectivity towards Cu^{2+} ions in the complex brain system even in the presence of interferences such as other metal ions and amino acids in a wide linear range of 1–60 μM . A detection limit of 100 nM was obtained.

Alizarin or alizarin red (AR) is another example of molecular receptors used for electrochemical sensing of vanadium ions in water samples (Amiri et al., 2013). For this purpose, AR was adsorbed on the surface of hydrophilic CDs with sulfonic functional groups via π – π stacking interactions. The sensing analysis was performed with square wave voltammetry and the prepared sensor was able to detect vanadium ion in range of 1–100 μM with detection limit of 96 nM.

2.10.2.3 g- C_3N_4 /CDs nanocomposite

The literature shows that very few researchers reported on the modification of glassy carbon electrodes with graphitic carbon nitride and carbon dots composite for electrochemical sensing. Yola et al. (2019) developed an electrochemical recognition system based on graphitic carbon nitride/N-doped carbon dots composite (g- C_3N_4 /CDs) and molecularly imprinted polymer for epinephrine detection. The epinephrine imprinted electrode showed high sensitivity for epinephrine recognition in wide linear range of 1×10^{-12} – 1.0×10^{-9} M, and detection limit of 3.0×10^{-13} M. CDs largely contributed to the increase of the electron transfer rate on the modified electrode. The epinephrine imprinted sensor was applied to urine samples for epinephrine analysis and the recovery percentage values ranged between 95.24% and 103.23% with relative standard deviation < 1.00.

2.11 Arsenic interferences

Detection of As (III) in water samples without interference is a challenging task since the other metal ions commonly present in the groundwater can be co-deposited and stripped off under the experimental condition used for the detection of As (III). The potential interferences which are commonly found in arsenic-contaminated samples were studied by Kim et al. (2016). It was reported that Cu was the most significant potential interference in the electrochemical detection of As (III). This interference may be explained by the possible formation of intermetallic compounds or alloys such as As-Cu during the electrode deposition step.

Ethylenediaminetetraacetic acid (EDTA) was used by several researchers when dealing with As detection interferences. Tiwari and Lee (2017) indicated that EDTA stabilized the arsenic speciation and also eliminated the interferences of manganese and iron for As (III). Zhou et al. (2017) achieved selectivity in detection of As (III) by adding 0.1 M EDTA for the removal of Cu^{2+} ions interference. Feeney and Kounaves (2000) reported that at a 1:1 concentration ratio, Pb(II), Hg(II), and Cu(II) caused a 10%, 30% and 65% respective decrease in the arsenic stripping current on Au ultramicro-electrode arrays.

Another study by Wen et al. (2018) was performed to evaluate the specificity of a developed biosensor towards the target As (III). The response of the biosensor was tested in aqueous solutions containing various common ions that may exist in lake water or underground water. The biosensor exhibits good selectivity toward the target As (III) with the other 15 interfering ions showing almost no response, except Hg^{2+} ions. The selectivity of the assay toward As (III) ion was improved further by the addition of a chelating ligand EDTA.

Cadmium was also documented to be one of the interfering ions in arsenic sensing (Dominguez-Gonzalez et al., 2014). Cadmium was reported as one of the significant cations that affects the peak current signal of arsenic during sensing. Ndlovu et al. (2014) documented the interference influence of cadmium on arsenic sensing, they discovered that addition of cadmium in the detection of arsenic resulted in a positive shift of the peak potential which had 8 % lower current than in the absence of cadmium.

CHAPTER 3

RESEARCH METHODOLOGY

In this chapter the materials and methods used during this study are highlighted with full description of the experimental setup and analytical procedures employed.

3.1 Materials

Disodium hydrogen phosphate (99.5%), sodium dihydrogen phosphate (99%), 2-chlorophenol (99%), phenol (99.5%), 4-chloro-3-methyl-phenol (99%), magnesium chloride hexahydrate (98%), manganese II sulfate (99%), cadmium nitrate trihydrate (99%), calcium hydroxide (95%) were purchased from Merck (Germiston, South Africa). Potassium ferrocyanide (99%), potassium nitrate (99%), lead nitrate (99.5%), zinc acetate (99.5%), silver nitrate (99.8%), were all purchased from Labochem (Johannesburg, South Africa). Sodium hydroxide (98%), sodium chloride (99%), cobalt nitrate (98%), cupric chloride dehydrate (98%), ethylenediaminetetraacetic acid (99%), ferric nitrate (98%) were purchased from ACE Chemicals (Johannesburg, South Africa). Potassium chloride (99.5%) was purchased from Glassworld (Johannesburg, South Africa). Dimethylformamide (99%) was purchased from Fisher Scientific (Johannesburg, South Africa). Hydrochloric acid (37%), thiourea (99%), iron chloride tetrahydrate (98%), 4-nitrophenol (99%), bisphenol A (99%), sodium meta arsenite (90%) and sulfamethoxazole (98%), were purchased from Sigma Aldrich (Johannesburg, South Africa). All chemicals were used without further purification. Phosphate buffer solution (PBS, 0.1 M, pH 7.6, 6 and 5 for 2-CP, As (III) and SMX respectively) was used as supporting electrolyte.

3.2 Preparation of nanomaterials

3.2.1 Preparation of carbon dots (CDs)

Pine cones which was the source for carbon dots synthesis, were collected from pine trees in Vanderbijlpark (26°42'37.91"S 27°51'39.35"E), Gauteng Province, South Africa. They were washed to remove impurities and some volatile organics such as resin acids and then dried in an oven at 80°C for 48 h. The pine cone scales were peeled and crushed to a powder using a pulveriser. After sieving, particles between 45 and 90 µm were obtained (Mabaso et al., 2018; Oseghe and Ofomaja, 2018).

CDs was prepared by a facile one-pot hydrothermal method using pine cone as the carbon source. Exactly 10 g of pine cone powder was dispersed in 50 mL ultrapure water. Then the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 24 h. After cooling, the solution was subjected to suction filtration to separate the filtrate from the residue. The aqueous solution was centrifuged at 8000 rpm for 20 min to separate the liquid from the deposition. The solution for C-dot preparation was obtained and then freeze-dried in vacuum for 48 h using a SCANVAC Cool-Safe freeze dryer. The final product was obtained as a brown powder which is highly soluble in water and hygroscopic.

3.2.2 Preparation of graphitic carbon nitride (g-C₃N₄)

Exactly 10 g of thiourea was weighed and transferred to an alumina crucible which was embedded with the CuO powder. Exactly, 5 mL of distilled water was added and the mixture was heated in a microwave oven at 600 W for 15 min. Then, the resultant powder was collected and calcined in air atmosphere in a tube furnace with a heating speed of 5°C/min to 550°C for 1 h. After calcination, a yellow powder was collected and named as g-C₃N₄ (Ma et al., 2016; Denisov et al., 2019; Zhang et al., 2020).

3.2.3 Preparation of g-C₃N₄/CDs nanocomposite

Exactly 10 g of thiourea was weighed and mixed with 5 mL of carbon dot solution (10 mg/mL). The mixture was poured into an alumina crucible and heated in a microwave oven at 600 W for 15 min. Then, the resultant powder was collected and calcined in air atmosphere in a tube furnace with a heating speed of 5°C/min to 550°C for 1 h. After calcination, a brown powder was collected and named as g-C₃N₄/CDs.

3.3 Characterization of synthesized nanomaterials

The synthesized materials were characterized using different analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) analysis and Transmission electron microscope (TEM). The electrochemical properties of the materials were investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

3.3.1 X-ray diffraction analysis (XRD)

The samples were ground into fine powder and a thin layer was prepared on a metal slide. The samples were placed on a sample holder inside the diffractometer. The X-ray powder diffraction patterns of CDs, g-C₃N₄ and g-C₃N₄/CDs were obtained using the Shimadzu-XRD 700 X-Ray Diffractometer where Cu target K α -ray (operating at 40 kV and 30 mA, $\lambda = 1.54056 \text{ \AA}$) was used as the X-ray source with a scan speed of 1°/minute. The divergence and convergence slit width was adjusted according to scanning range of 2 θ before scanning.

3.3.2 Fourier-transform infrared spectroscopy (FT-IR)

FT-IR was used to identify the functional groups present in the synthesized materials in the range of 600-4000 cm⁻¹. FT-IR spectra of bond vibrations of synthesized materials were analysed on Fourier transform infrared spectrophotometer machine (Perkin Elmer spectrum 400).

3.3.3 Transmission electron microscope (TEM)

Surface morphologies of the materials (CDs, g-C₃N₄ and g-C₃N₄/CDs) were studied by transmission electron microscope (JEOL JEM-2100) at 200 kV).

3.3.4 Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) analyses

Electrochemical analyses were conducted on a BioLogic SP-240 potentiostat electrochemical workstation. Bare electrode (GCE), CDs/GCE, g-C₃N₄/GCE and g-C₃N₄/CDs/GCE sensors were electrochemically characterized using CV and EIS.

All electrochemical experiments were carried out at room temperature using a three-electrode system. A modified bare GCE electrode and a platinum wire served as the working (WE) and counter electrodes (CE), respectively. An Ag/AgCl electrode was used as the reference electrode (RE). CV and EIS analyses were run by immersing the three electrodes in an electrochemical cell containing ferrocyanide solution ([Fe (CN) 6]^{3-/4-} and 0.1 M KCl) as the redox marker. CV was done by cycling a potential from -800 mV to 200 mV at a scan rate of 50 mV/s and then the peak current signal of the bare GCE and the modified working electrodes were compared.

EIS is a powerful technique for characterization of the electrical properties of modified electrodes. The parameters for EIS analysis were as followed: frequency range from 100 kHz to 40 mHz, sinus amplitude = 5 mV and period before each measurement (P_w) = 0.1. The EIS data were analyzed using Z fit software.

3.4 Experimental details for 2-chlorophenol, arsenic and sulfamethoxazole sensing

3.4.1 Preparation of the working electrode

Before modification, the bare GCE was polished to a mirror-like appearance with 1 then 0.05 μ m alumina slurry, then washed successively with anhydrous alcohol and redistilled water in an ultrasonic bath for 1 min, and then dried. The working electrode was prepared as follows: 15 μ L

of g-C₃N₄/CDs dispersion was added onto the prepared GCE surface and dried. The obtained electrode was referred as g-C₃N₄/CDs/GCE. The modification of GCE with other materials followed a similar procedure (Yu et al., 2016).

3.4.2 DPV experimental procedure for analytes detection

For 2-CP sensing, the modified electrode (WE), CE and RE were immersed in 10.0 mL of 0.1 M phosphate buffer (pH = 7.6) containing a concentration range from 2 to 10 μ M and from 0.5 to 2.5 μ M of 2-CP, then the three electrodes were dipped into the electrochemical cell and a potential was applied to the solution from the potentiostat. Then differential pulse voltammograms were recorded and the peak currents were read. The parameters for differential pulse voltammetry analysis are as follows: scan rate = 10 mV/s, applied potential from 0 V to 0.8 V, pulse height = 25 mV, step height = 5 mV, pulse width = 100 ms and step time = 0.5 s. Arsenic and sulfamethoxazole were detected following similar procedure parameters except for the potential window which was altered from -0.2 to 1.2 V and from 0 to 1.5 V for arsenic and sulfamethoxazole, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

Electrochemical detection of 2-chlorophenol at carbon dots-graphitic carbon nitride modified glassy carbon electrode

4.1 Characterization of the CDs, g-C₃N₄, and g-C₃N₄/CDs nanomaterials

4.1.1 Structural and morphological characterization of CDs, g-C₃N₄, and g-C₃N₄/CDs

4.1.1.1 X-ray powder diffraction (XRD)

XRD patterns were utilized for identifying and determining the different phase structures of the synthesized samples. **Figure 4.1** shows the XRD patterns of CDs, g-C₃N₄ and g-C₃N₄/CDs nanomaterials.

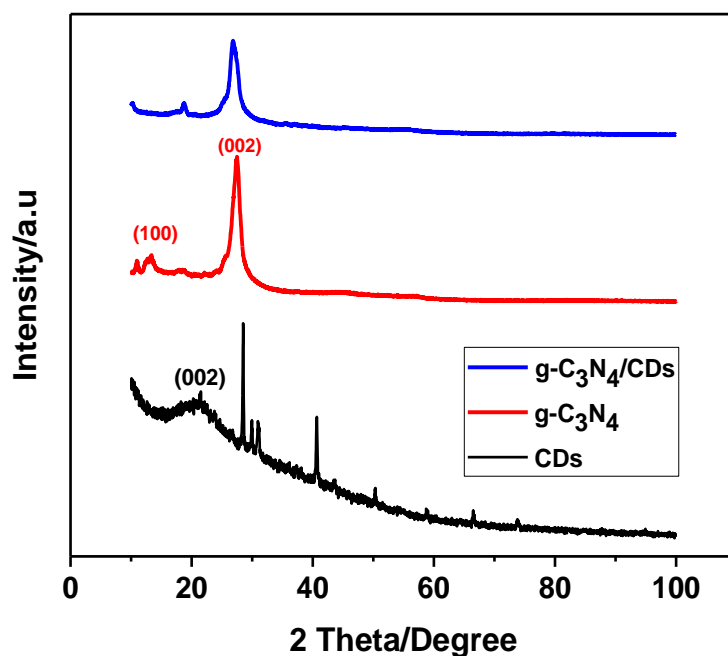


Figure 4. 1 XRD pattern of CDs, g-C₃N₄ and g-C₃N₄/CDs.

The XRD pattern of CDs (**Figure 4.1**), showed a broad diffraction peak at about $2\theta = 20.96^\circ$ which refers to the characteristic lattice plane (002) from a normal graphene sheet. This indicates that CDs are amorphous in nature which is due to closely packed carbon atoms with alkyl chains. A greater number of oxygen and nitrogen containing groups on CDs are characteristic of the amorphous nature of CDs (Kumar et al., 2017).

The g-C₃N₄ sample exhibited two pronounced peaks at 27.56° and 13.35° . The peak at 27.56° can be indexed as the (002) plane corresponding to the diffraction signal of graphitic carbon materials which comes from the interlayer stacking of aromatic segments, (JCPDS card no 066-0813) (Lavkush Bhaisare et al., 2015). The peak at 13.35° can be indexed as the (100) planes which comes from in-plane structural repeating units of tri-s-triazine (Tashkhourian et al., 2018).

From the XRD pattern of the g-C₃N₄/CDs nanocomposite the characteristic peak of g-C₃N₄ is observed and left shifted to 27.57° with less intensity due to the added CDs. Additionally, the characteristic peaks of CDs can also be observed with less intensity and left shifted to 18.76° with no broadness. Hence, this suggests that incorporation of CDs on the surface of g-C₃N₄ was accomplished.

4.1.1.2 Fourier-transform infrared spectroscopy (FT-IR)

The FTIR spectra of CDs, g-C₃N₄ and g-C₃N₄/CDs are shown in **Figure 4.2**.

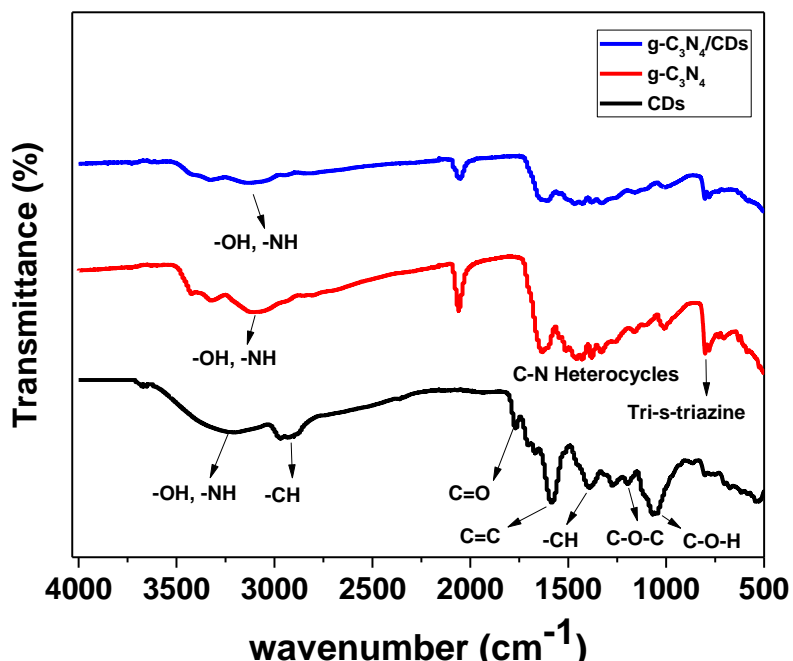


Figure 4. 2 FTIR spectrum of CDs, g-C₃N₄ and g-C₃N₄/CDs

The functional groups of the CDs can be observed and the broad peak at 3204 cm⁻¹ is ascribed to stretching vibration of O-H and N-H. The peaks at 2970 cm⁻¹ and 1393 cm⁻¹ correspond to the stretching vibration of aliphatic carbon and bending vibration of C-H, respectively (Jiayi Qin and Zeng, 2017; Wang et al., 2017; Yola and Atar, 2019). The band at 1768 cm⁻¹ is assigned to C=O stretching vibration combined with the peaks derived from C-O (C-O-C and C-O-H) stretching modes at 1197 and 1066 cm⁻¹, respectively. This demonstrates the presence of surface groups such as hydroxyl, carboxyl and carbonyl on CDs (Li, 2006; Jiayi Qin and Zeng, 2017; Wang et al., 2017). The peak at 1584 cm⁻¹ corresponds to the stretching mode of C=C (Kumar et al., 2017).

For pure g-C₃N₄, several peaks in the region of 1300–1650 cm⁻¹ (the peaks occur at about 1331, 1380, 1428, and 1632 cm⁻¹) are observed and are assigned to the typical breathing modes of C-N heterocycles (Yola and Atar, 2019). Additionally, the band at 801 cm⁻¹ is assigned to the

characteristic breathing mode of tri-s-triazine units (Jiayi Qin and Zeng, 2017), while the broad band at around 3103 cm^{-1} is indicative of N-H vibration of the uncondensed amine groups and O-H stretching vibration modes (Jiayi Qin and Zeng, 2017; Lee et al., 2017; Wang et al., 2017).

The characteristic peaks observed with the g-C₃N₄/CDs nanocomposite showed a reduction in the peaks intensity found in the g-C₃N₄ and CDs. Hence, the difference of intensity confirmed the formation of the g-C₃N₄/CDs nanocomposite.

4.1.1.3 Transmission electron microscope (TEM)

The morphologies of CDs, g-C₃N₄ and g-C₃N₄/CDs were investigated by TEM (**Figure 4.3 A, B, C**). The electron images of CDs (**Figure 4.3 A**) show well-dispersed particles, while the image of g-C₃N₄/CDs (**Figure 4.3 B**), reveal sheets structure with many voids and pores. The TEM image of g-C₃N₄/CDs (**Figure 4.3 C**), showed regions of dense dark spot embedded in the g-C₃N₄ nanosheets, but CDs cannot be distinguishably observed.

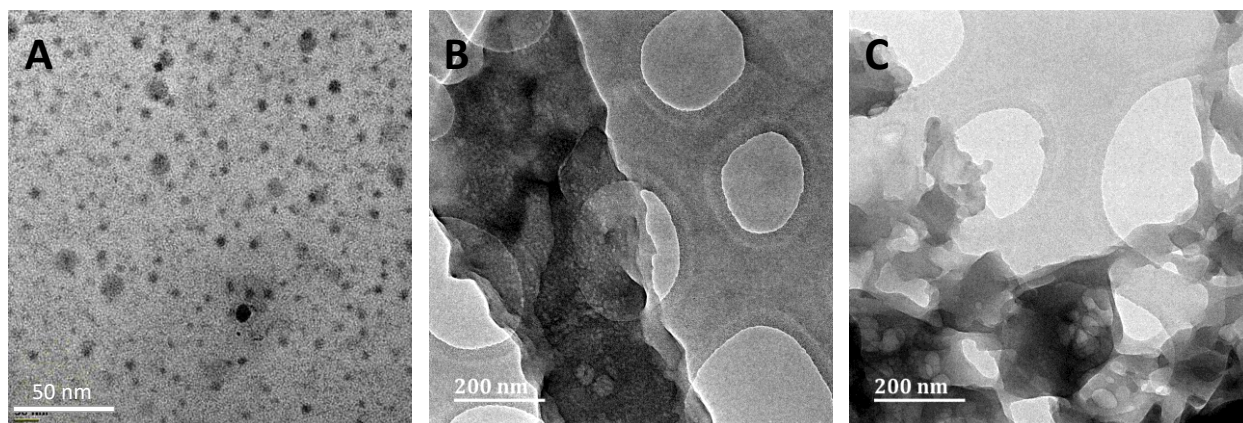


Figure 4. 3 TEM images of CDs (A), g-C₃N₄ (B) and g-C₃N₄/CDs (C)

4.1.2 Electrochemical characterizations of electrodes

4.1.2.1 Cyclic voltammetry (CV)

Electrochemical properties of the fabricated electrodes were explored in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl as a supporting electrolyte solution. As displayed in **Figure 4.4**, the higher peak current for the g-C₃N₄/GCE and CDs/GCE electrodes compared to the bare GCE indicates that the electron transfer on the fabricated electrodes was enhanced. From the voltammogram, a pair of well-defined redox peaks on g-C₃N₄/CDs/GCE with higher redox peak currents in comparison with other electrodes was observed. The peak current was maximum at the g-C₃N₄/CDs/GCE suggesting a good synergy between CDs and g-C₃N₄ as evidenced from the XRD and FTIR analysis described above.

In the case of GCE, the oxidation peak was observed at a potential of -65 mV with a peak current of 39 μA and the reduction potential was obtained at -196 mV with peak current -48.7 μA . In comparison with GCE, the modified electrode g-C₃N₄/CDs/GCE illustrated higher oxidation (59 μA) and reduction currents (-69 μA) with a slight shift in potential to the left (-70 mV \rightarrow - 83 mV). The increase in peak current and shift in peak potential confirmed the better electrocatalytic activity of the fabricated g-C₃N₄/CDs/GCE electrode (Shereema et al., 2018; Yola and Atar, 2019).

The increase in current was also attributed to good electronic conductivity and an increase in electroactive surface area of the g-C₃N₄/CDs/GCE electrode which enhanced the sensitivity of the electrode for electroanalysis (Thabile Ndlovua et al., 2014; Hanqiang Zhang et al., 2015). The electroactive surface areas were calculated using the Randles-Sevcik equation:

$$i_p = 2.69 \times 10^5 n^{3/2} v^{1/2} D^{1/2} A C \dots\dots\dots \text{(Equation 4.1)}$$

Where n is the number of electrons, V (mV/s) is the scan rate, A (cm²) the area of the electrode, C is the concentration in mol/L and D (cm²/s) is the diffusion coefficient of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl which has been reported to be 6.3×10^6 cm²/s and i_p (A), the peak current. The g-C₃N₄/CDs/GCE had the largest active surface area of 0.082 cm² compared to 0.072 cm², 0.064 cm² and 0.052 cm² for CDs/GCE, g-C₃N₄/GCE and bare GCE, respectively. This high surface area is attributed to the synergistic interaction between CDs and g-C₃N₄.

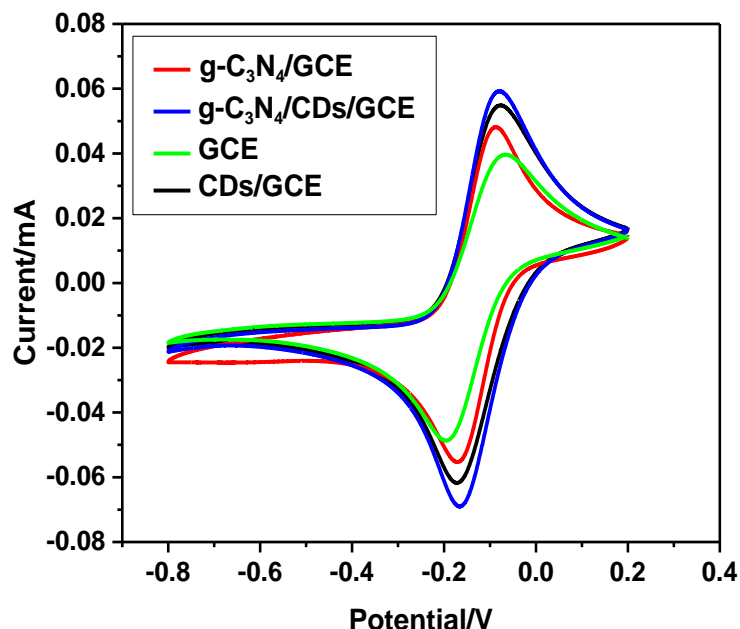


Figure 4. 4 CV of GCE, CDs/GCE, g-C₃N₄/GCE and g-C₃N₄/CDs/GCE in 5mM [Fe (CN) 6]^{3-/4-} containing 0.1 M KCl at scan rate of 50 mV/s

The kinetic parameters of the electron-transfer reactions at the electrode surfaces were studied. Scan rates were studied from 10 to 100 mV/S with modified g-C₃N₄/CDs/GCE surface, using 5 mM ferrocyanide solution dissolved in 0.1 M KCl electrolyte. As shown in **Figure 4.5 A**, both anodic and cathodic peak currents were found to be proportional to the scan rate in the range between 10 and 100 mV/s. The anodic peak potentials (E_{pa}) became slightly more positive whereas the cathodic peak potentials (E_{pc}) became more negative with increasing scan rates. The scan rate study shows that the interfacial kinetics is diffusion-controlled because the peak current is proportional to the square root of scan rate in **Figure 4.5 B**. Diffusion-controlled kinetics suggest that the concentration of an analyte can be deduced from the change in current of the system (Ndlovu et al., 2014; Xu et al., 2018).

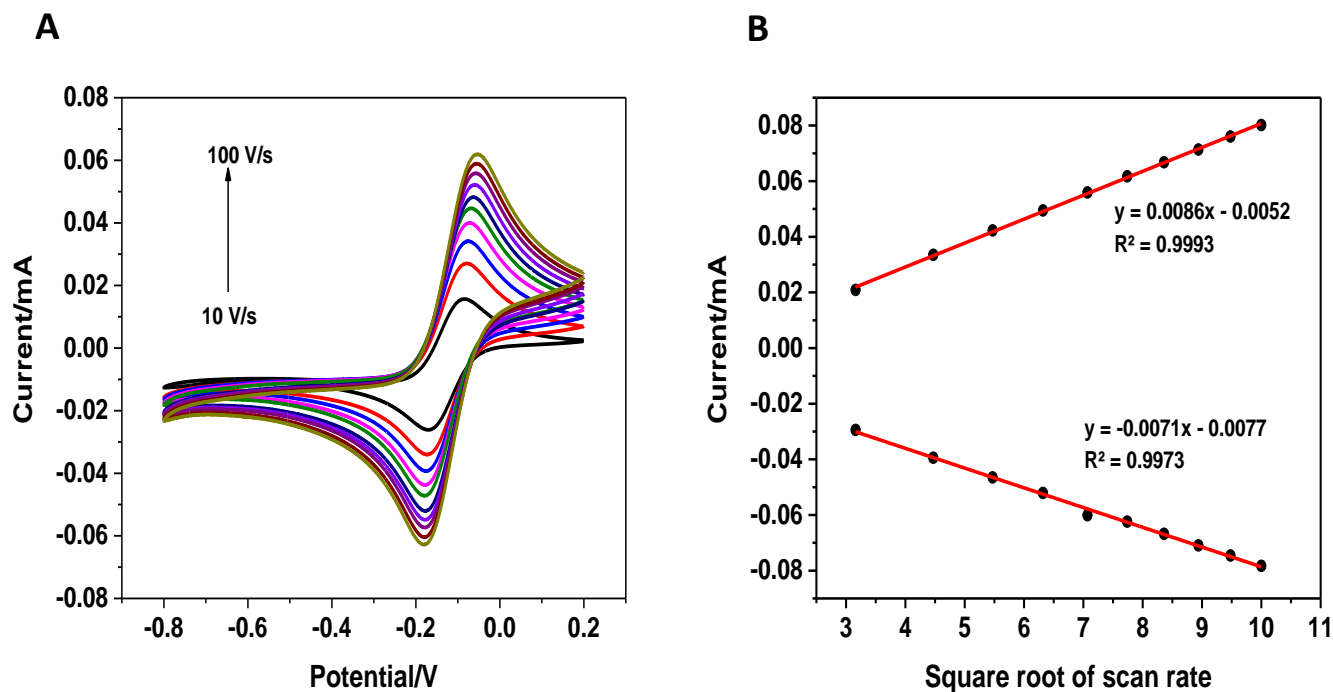


Figure 4. 5 (A) CV of varying scan rates of g-C₃N₄/CDs/GCE in 5mM [Fe (CN) 6]^{3-/4-} containing 0.1 M KCl. (B) The linear plot of peak currents vs square root of scan rate

4.1.2.2 Electrochemical impedance spectroscopy (EIS)

The electrical properties (charge transfer resistance) of different modified electrodes were investigated by EIS on the surface of different modified electrodes in the presence of 5 mM of [Fe(CN) 6]^{3-/4-}. The resulting plots are depicted in **Figure 4.6** and shows the EIS Nyquist plots of bare and modified GCE electrodes. All the EIS curves consist of two portions: a semicircle portion reflecting the electron-transfer resistance (R_{ct}) at high frequencies and a linear portion representing the diffusion process at low frequencies (Zhanga et al., 2015; Xu et al., 2018).

The Randles equivalent circuit (**inset of Figure 4.6**), comprising of R1 which corresponds to the uncompensated resistance of the electrolyte (R_s) and Q2 corresponds to the electrical double layer capacity which is proportional to the real surface area of the electrode. The R2 value corresponds to the charge transfer resistance (R_{ct}) for the faradic reactions taking place at the open circuit potential. The Warburg element in the circuit, W2, is the well-known diffusional element for the ionic species at the interface (Carrera et al., 2017).

The large semicircular portion of the bare GCE suggests a poor interfacial charge transfer with R_{ct} value of 766 Ω . The R_{ct} value decreased to 292 Ω for the g-C₃N₄/GCE, which indicates that g-C₃N₄ enhanced the electron transfer. The R_{ct} value further declined to 27 Ω and then to 13 Ω on CDs/GCE and g-C₃N₄/CDs/GCE, respectively, suggesting a better electron transfer on those electrodes. The synergistic effect of g-C₃N₄ and CDs showed that the g-C₃N₄/CDs/GCE electrode displayed the highest conductivity thus promoting the fast electron transfer process with a negligible semicircle domain in the Nyquist plot (Zhu et al., 2018; Zhimin et al., 2020).

Lower impedance is expected if more charges or electrons are exchanged as observed in the g-C₃N₄/CDs/GCE electrode (Thabile Ndlovu et al., 2014). The almost linear Nyquist plot of g-C₃N₄/CDs/GCE indicated that the coupling of CDs and g-C₃N₄ can significantly improve the electron transfer rate (Yu et al., 2016). The corresponding R_{ct} values obtained for the electrodes are consistent with CV results obtained in **Figure 4.4**. Based on the present analysis, g-C₃N₄/CDs/GCE would have a better response for analytes sensing in this study.

Based on CV and EIS results we concluded that the g-C₃N₄/CDs/GCE electrode was the most suitable one for our sensing analysis due to its high surface area and lower resistance to electron transfer.

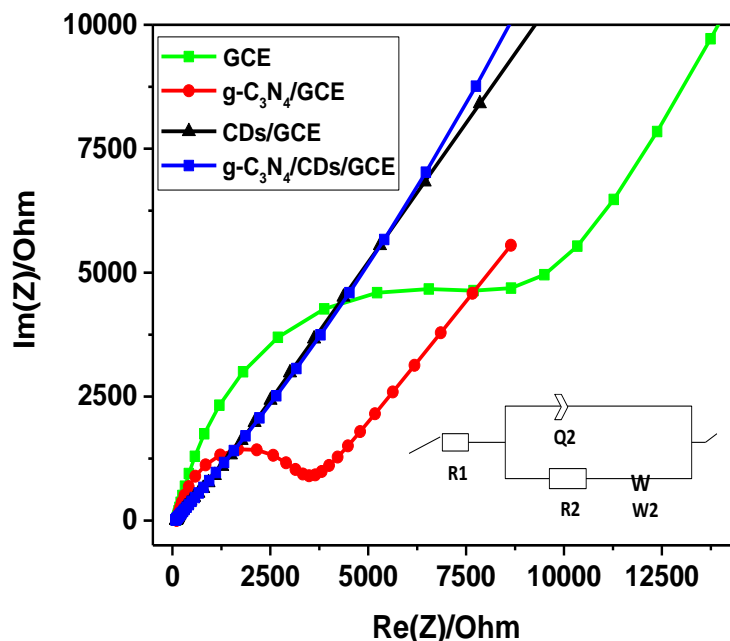


Figure 4. 6 Nyquist plots and equivalent circuits (insert) of GCE, CDs/GCE, g-C₃N₄/GCE and g-C₃N₄/CDs/GCE at a scan rate of 50 mV/s in 5mM [Fe (CN) 6]^{3-/4-} containing 0.1 M KCl

4.2 Optimization: The effect of pH and amount of g-C₃N₄/CDs suspension for the determination of 2-chlorophenol

4.2.1 The effect of pH value

The development of a sensitive sensor usually requires the optimization of some influencing factors such as the pH. pH not only influences the transfer of proton of the redox process but also influences the interaction between the modifier of the electrode surface and the analyte and this has a significant effect on the electrochemical behaviors of analytes (Liang et al., 2016). Optimal pH for analysis is fixed as the one which gives a stable voltammogram with lower peak potential and enhanced current response (Theresa, 2015). The influence of pH on the oxidation of 2-CP on g-C₃N₄/CDs/GCE was studied from pH 4.0 to 7.6 with DPV in 0.1 M PBS (**Figure 4.7**). The current intensity of the oxidation peak reached its maximum at pH 5 and lowest potential at pH 7.6 while the oxidation peak potential decreased with the increased of pH. Therefore, PBS with

pH 7.6 was used as the supporting electrolyte in all determinations because of a low potential (0.4 V).

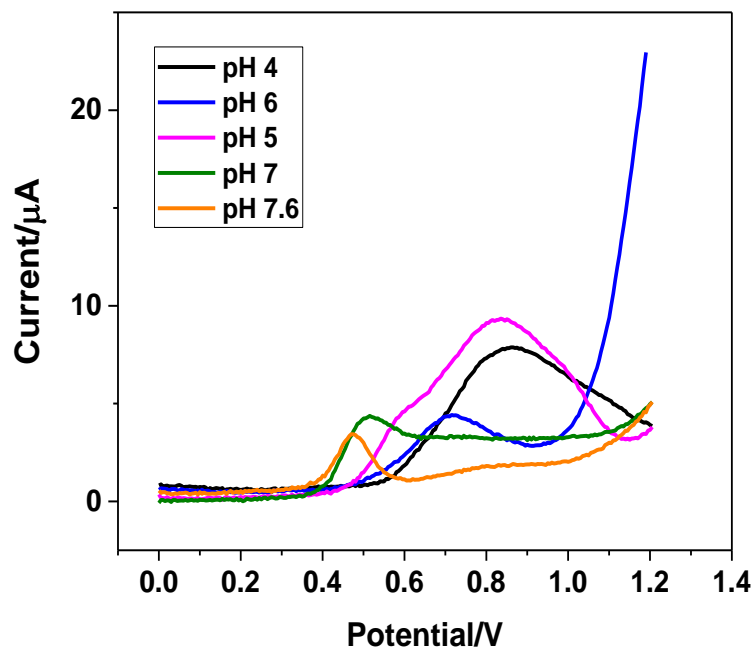


Figure 4. 7 DPV plots of 2 μ M 2-CP on g-C₃N₄/CDs/GCE in 0.1 M PBS at different pH values

4.2.2 The effect of the amount of g-C₃N₄/CDs suspension

The relationship between the volume of g-C₃N₄/CDs suspension onto the bare GCE surface and the oxidation peak current of 2-chlorophenol was examined with DPV. **Figure 4.8**, demonstrates that the oxidation peak current of 2-chlorophenol gradually increases with increasing volume of g-C₃N₄/CDs suspension from 5 to 15 μ L. However, the oxidation peak current conversely decreased when the g-C₃N₄/CDs suspension exceeded 15.0 mL. The volume of g-C₃N₄/CDs suspension on the GCE surface was kept at 15 μ L in the present study.

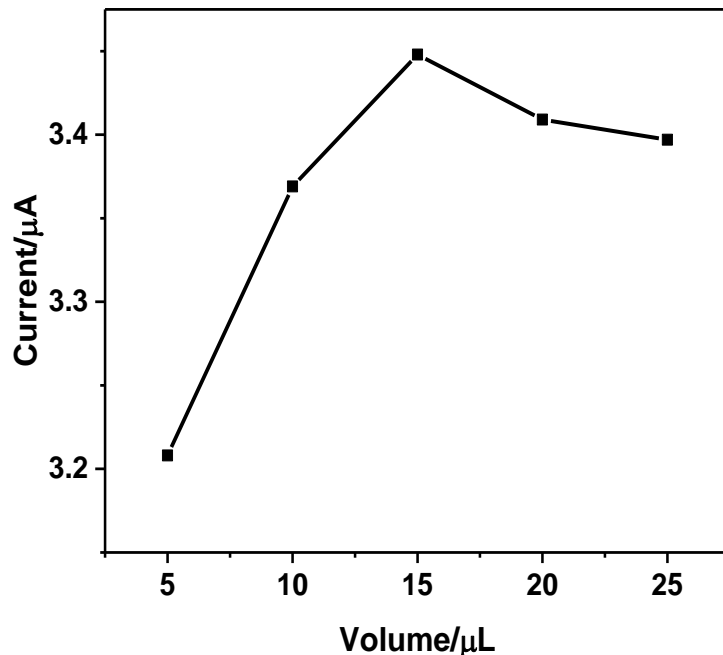


Figure 4. 8 Effect of pH on the oxidation current and potential of 2 μ M 2-CP in 0.1 M in PBS on g-C₃N₄/CDs/GCE at a scan rate of 50 mV/s in 5mM [Fe (CN) 6]^{3-/4-} containing 0.1 M KCl

4.3 Electrochemical behaviors of 2-CP at different electrodes

The electrochemical behavior of 2-CP at different modified electrodes was investigated by the DPV technique and shown in **Figure 4.9**. The GCE, g-C₃N₄/CGE and CDs/CGE electrodes showed weaker oxidation peaks compared to the g-C₃N₄/CDs/CGE electrode which displayed the highest oxidation peak current. The modification of the g-C₃N₄/CGE electrode with CDs had a large effect on the oxidation current of 2-CP, which increased greatly with a current intensity 45% higher than that registered on the g-C₃N₄/CGE electrode, while the oxidation potential remained almost the same. The results indicated that CDs promotes binding with 2-CP, possess good electrochemical activity towards the oxidation of 2-CP and greatly amplified the peak current perhaps due to its high conductivity. The increase in the electrochemical performance and catalytic activity of g-C₃N₄/CGE may be due to the synergistic effect between the g-C₃N₄ and CDs as well as the strong interaction between the active sites of g-C₃N₄/CDs and 2-CP molecules (Yu et al., 2016; Asadian et al., 2019). The results are consistent with the results obtained by CV.

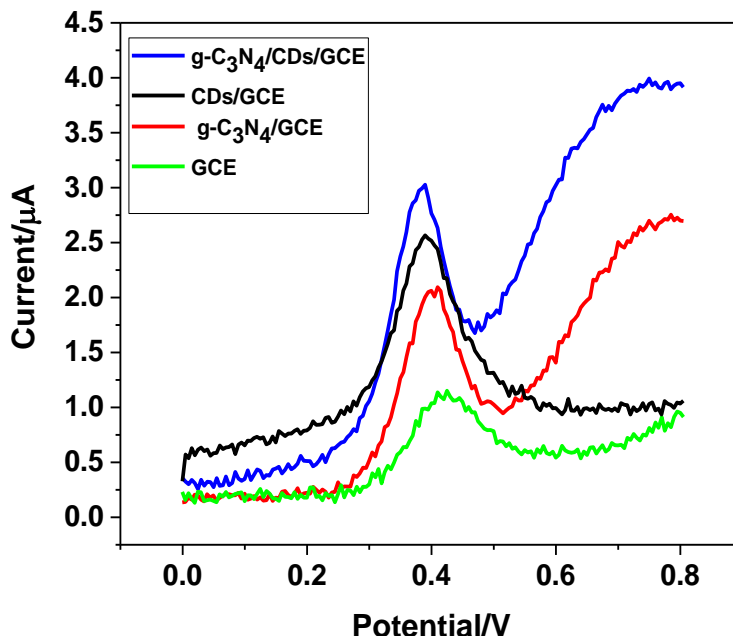


Figure 4. 9. DPV of GCE, g-C₃N₄/CGE, CDs/GCE and g-C₃N₄/CDs/CGE in 0.1 M PBS (pH = 7.6) containing 2 μM of 2CP

4.4 Voltammetric determination of 2-chlorophenol

Due to its higher current sensitivity and better resolution than CV, DPV was utilized for the determination of 2-chlorophenol with the g-C₃N₄/CDs/GCE electrode under the optimized conditions in PBS (pH = 7.6) (Yu et al., 2016).

Figure 4.10 shows that the oxidation peak of 2-chlorophenol increases linearly with 2-chlorophenol concentration ranging from 0.5 to 2.5 μM and from 2 to 10 μM. A linear calibration curve was obtained for each concentration range, 2 -10 μM (Figure 4.9 C); $I_{pa} (\mu A) = 0.5879 C (\mu M) + 1.9799$ and from 0.5 to 2.5 μM (Figure 4.9 D); $I_{pa} (\mu A) = 0.8198 C (\mu M) + 1.9899$. Based on the recommended $3\sigma/m$ method in which σ is the standard deviation of a set of measurements at lowest concentration level and m is the slope of the calibration plot, the Limit of Detection (LOD) was calculated as 0.62 μM with average peak potential of 0.43 V.

The good sensing performance of g-C₃N₄/CDs can be attributed to a good conductivity and electrocatalysis of CDs as well as the presence of several nitrogen atoms on the surface of g-C₃N₄

which can provide more electrochemical active sites to improve the electrochemical activity of the materials (Zhao et al., 2017). The good combination and the π -conjugation of CDs with g-C₃N₄ may have played an important role in enabling the quick electron transfer inside the g-C₃N₄/CDs nanocomposite and exhibiting significant synergistic effects (Xu et al., 2018).

Such analytical performance indicates that the g-C₃N₄/CDs nanocomposite is likely to act as a highly sensitive 2-chlorophenol sensor. Compared to other electrochemical sensors in **Table 4.1**, the proposed g-C₃N₄/CDs/GCE showed good sensitivity and registered a lower peak potential. The fabrication process of the electrode was simpler and in addition carbon dots have low toxicity making it possible to represent a new platform for designing environment-friendly electrochemical sensors.

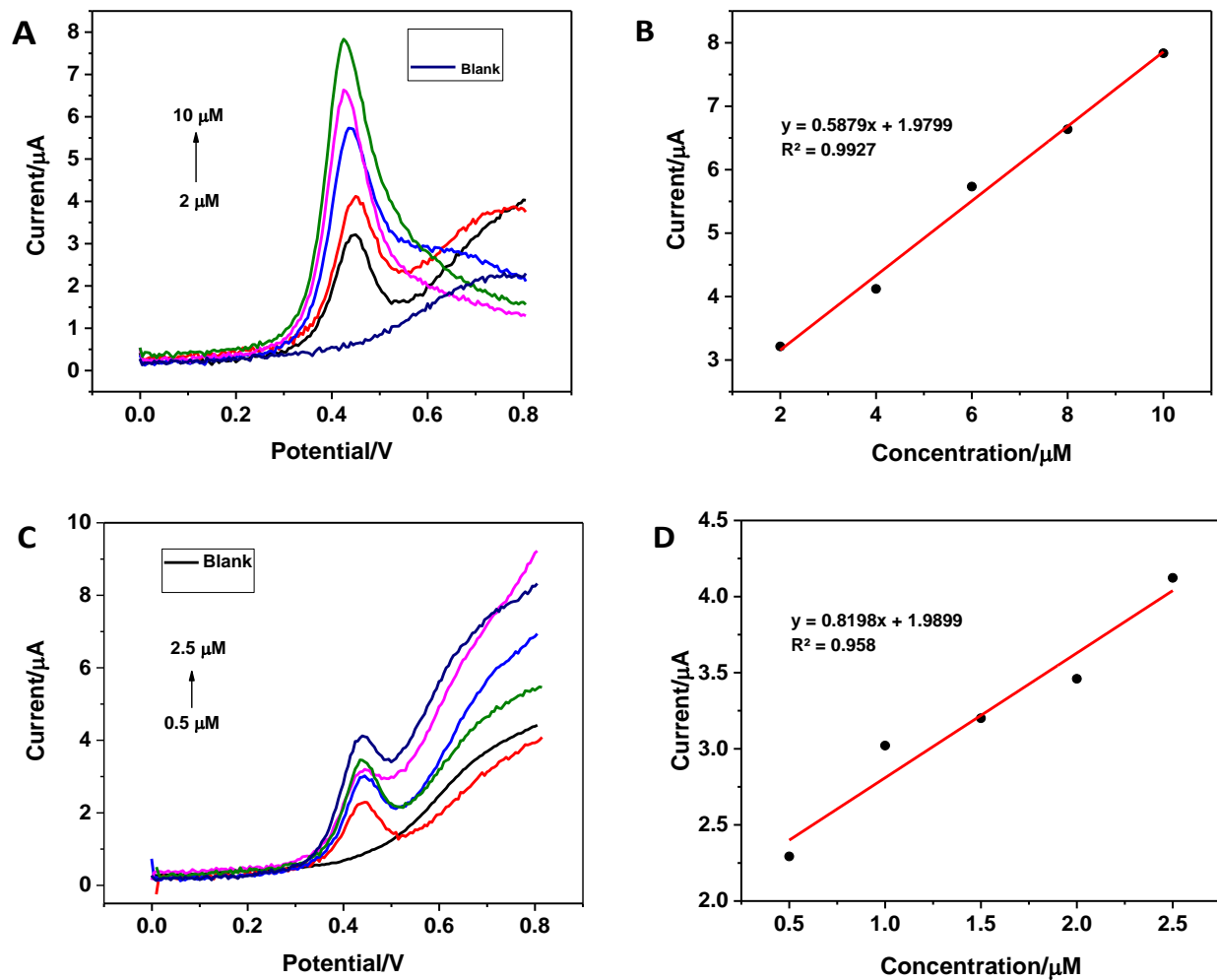


Figure 4. 10 DPV plots of 2-CP with various concentrations at g-C₃N₄/CDs/GCE in 0.1 M PBS (pH = 7.6): (A) 2-10 μM (B) 0.5-2.5 μM. The linear relationship between oxidation peak current and the concentration of 2-CP from (C) 2 to 10 μM; (D) 0.5 to 2.5 μM

Table 4. 1 Comparative study on the performance of different electrochemical sensors for 2-chlorophenol detection

Sensors	Linear range (μM)	Limit of Detection (μM)	pH	Oxidation potential (V)	References
AB-DHP/GCE	0.2 – 40	0.05	7	0.62	(Dong and Huajie, 2006)
f-CNTs/ RhB/GCE	0.05 – 125	0.028	3	0.74	(Zhu et al., 2018)
CD/GRs/CPE	0.5-40	0.2	5.5	0.78	(Maochao Wei et al., 2014)
HRP-SDBS-HT-GC	0.005-0.05	0.002	7		(Fernández et al., 2013)
IL-Pd-graphene	4 - 800	1.5	7.4	0.6	(Shi and Zhu, 2011)
MWNT-DCP film-coated GCE	0.1 – 20	0.04	6	0.63	(Li, 2006)
ZnSe-CTAB/CS/GCE	0.02-10	0.008	6	0.8	(Lia et al., 2013)
g-C₃N₄/CDs/GCE	0.5 – 2.5	0.62	7.6	0.43	This work

4.5 Reproducibility and stability of the g-C₃N₄/CDs/GCE sensor

4.5.1 Reproducibility

The reproducibility of the g-C₃N₄/CDs/CGE was investigated by measuring the response to 2 μ M 2-CP in 0.1 M PBS (pH=7.6). The electrode reproducibility was estimated by using five modified electrodes that were prepared under the same conditions. The intensity of the current peaks were almost equal to each other with a RSD of 8.13% (**Figure 4.11**), revealing good reproducibility of the fabricated g-C₃N₄/CDs/CGE sensor.

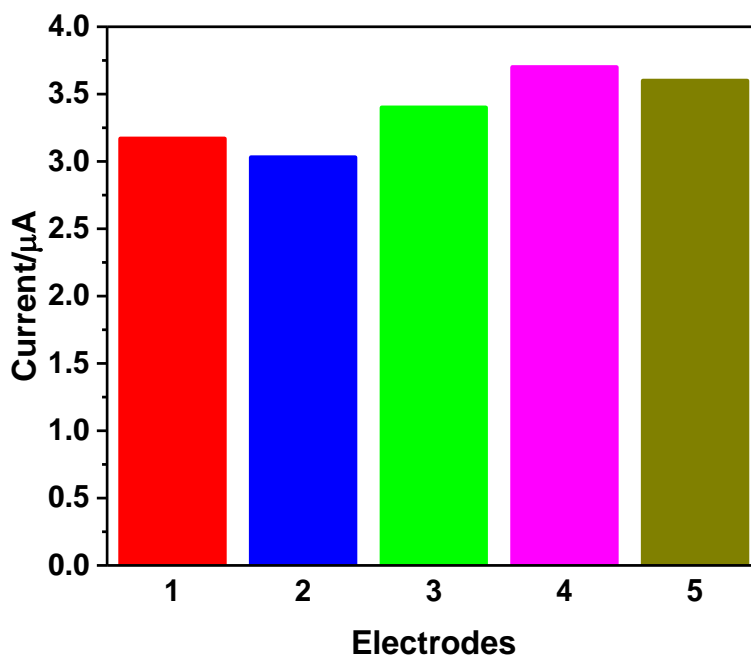


Figure 4. 11 Reproducibility of g-C₃N₄/CDs/CGE modified electrode with five different DPV response measurements for 2 μ M 2-CP in 0.01 M PBS at pH 7.6

4.5.2 Stability

The stability of the sensor was evaluated by storing the fabricated electrode at 4°C for two weeks. The electrode was then used for the determination of 6 μM 2-CP every third day. The response peak current dropped to 50% after one week and to about 15% after two weeks (**Figure 4.12**). The electrode remained active for two weeks but there was a decrease of the electrochemical performance over time leading to a poor stability. This is probably due to the detachment of the nanocomposite from the electrode surface into the solution each time the sensing analysis was performed (Lia et al., 2013).

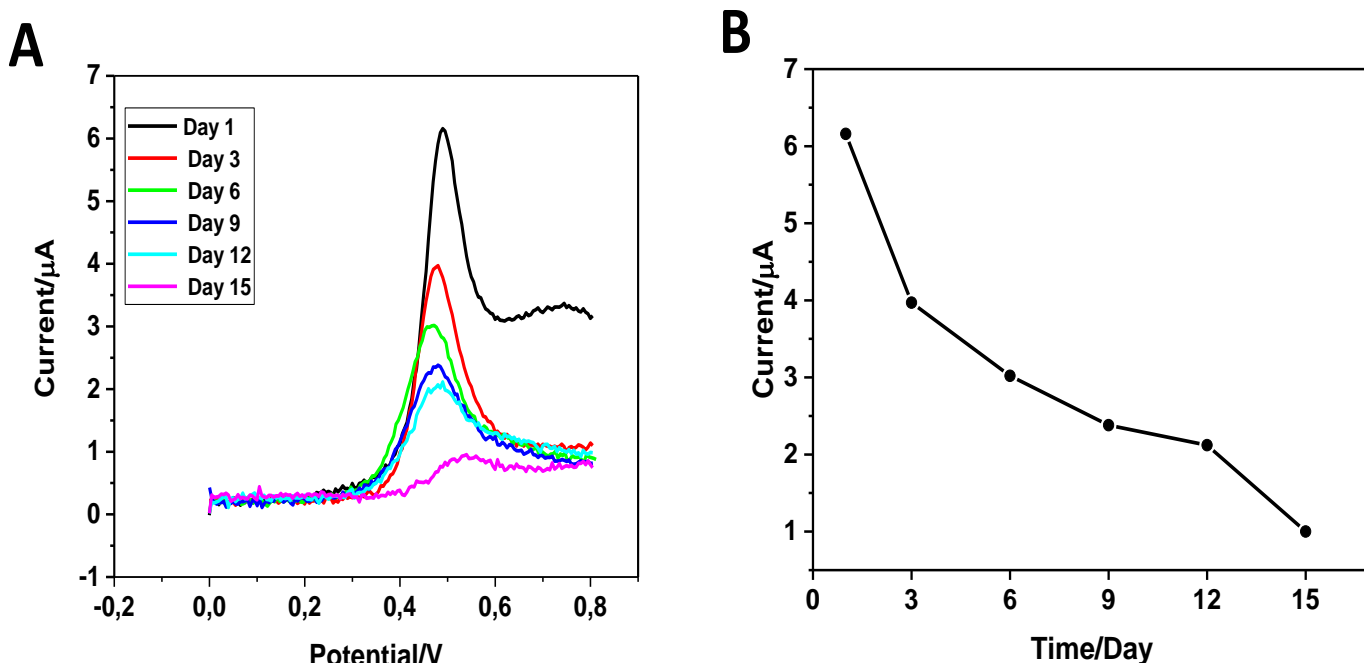


Figure 4. 12 (A) Stability of g-C₃N₄/CDs/CGE modified electrode with repetitive measurements of DPV response over two weeks for 4 μM 2-CP in 0.01 M PBS with pH 7.6, (B) Relationship between current and time

4.6 Interferences studies

A drawback of 2-chlorophenol detection using voltammetry or amperometric methods is that it could be susceptible to interferences from various compounds which are oxidized at the same or almost the same potential with it. This leads to an increase in the peak current of 2-chlorophenol. To study the effect of potential interfering compounds/species on the oxidation peak current of 2-chlorophenol, a 2 μM concentration of it was used and a 5-fold higher concentration of each potentially interfering species/molecule was added. A wide range of inorganic ions including Cd^{2+} , Hg^{2+} , Fe^{2+} , Pb^{2+} , As^{3+} , Zn^{2+} , Mn^{2+} , Fe^{3+} , Ag^{+} , Na^{+} , Mg^{2+} and Ca^{2+} did not have a substantial influence on the current signal of 2-chlorophenol. The addition of a 5-fold higher concentration of the ions caused less than 5% change in the signal of the analyte. Furthermore, phenol and some substituted phenols such as bisphenol A, 4-nitrophenol and 4-chloro-3-methylphenol were also tested for their effects on the 2-chlorophenol current signal. It was found that 4-nitrophenol and bisphenol A, did not interfere significantly with the oxidation signal of 2-chlorophenol, but phenol and 4-chloro-3-methylphenol caused signal changes of about +10 and +65%, respectively (see **Table 4.2**).

Table 4. 2 Interferences of inorganic and organic species on the determination of 2.0×10^{-3} mM 2-chlorophenol

Interfering ions	Concentration (mM/L)	Signal change (%)
Fe³⁺	0.01	+4.26
Mn²⁺	0.01	+1.10
Cd²⁺	0.01	+1.15
As³⁺	0.01	+1.64
Ag⁺	0.01	+1.37
Ca²⁺	0.01	+1.94
Fe²⁺	0.01	+4.08
Pb²⁺	0.01	+4.16
Na⁺	0.01	+1.42
Mg²⁺	0.01	+3.43
Zn²⁺	0.01	+1.43
Bisphenol A	0.002	-2.7
4-Nitrophenol	0.002	+1.67
Phenol	0.002	+10.45
4-chloro-3-methylphenol	0.002	+65.47

4.7 Analysis of water samples

To assess the suitability of the proposed sensor for real life application, water samples were collected from a river in the Vanderbijlpark and from water tap in the University (Vaal University of Technology, Vanderbijlpark Campus). Prior to analyses, the water samples were prepared with PBS such that the final solution has 0.1 M PBS, pH 7.6. **Figure 4.13** showed no obvious DPV electrochemical response between 0.2 and 0.8 V for the effluent and tap water samples. It was

assumed that the concentration of 2-chlorophenol of the effluent and tap water was too low to be detected.

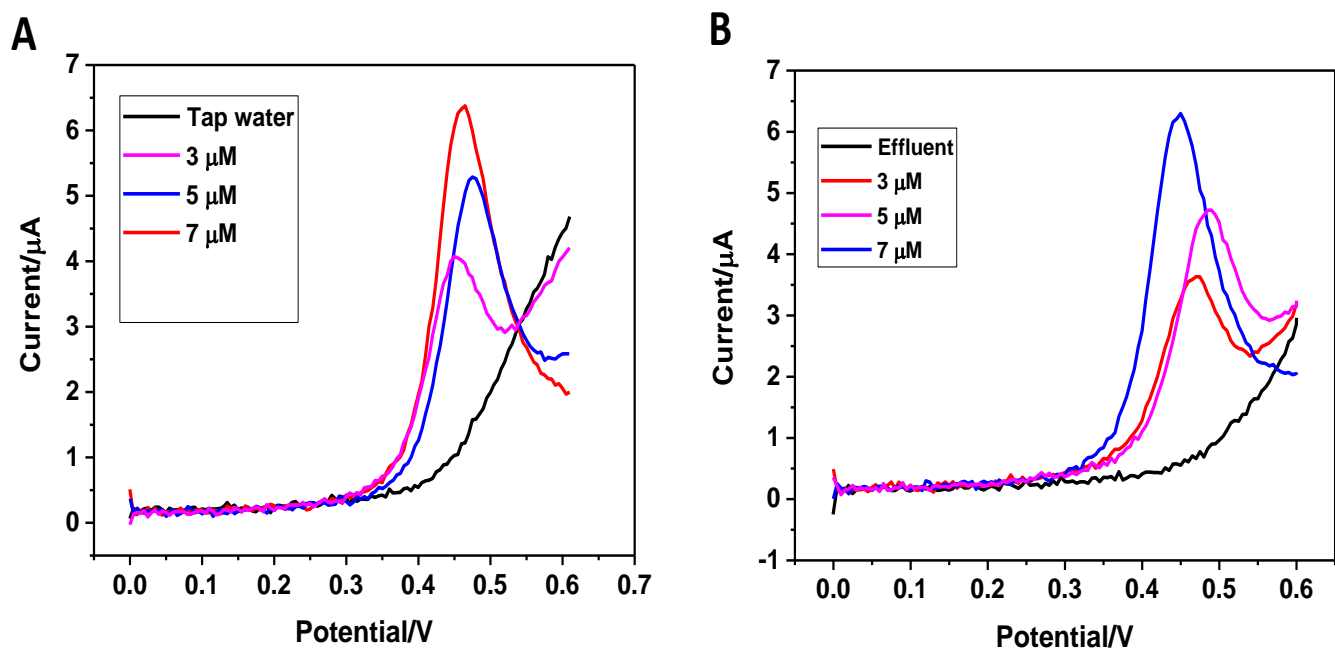


Figure 4. 13 DPV plots of 2-CP detection in real water sample (A) Tap water (B) Effluent

Known concentrations of 2-chlorophenol at three concentration levels (3, 5 and 7 μM), were added to the effluent and tap water samples and detected by DPV method. The results are shown in **Table 4.3**. The percentages of recovery of 2-chlorophenol were between 93% and 118%, showing that the proposed method is acceptable for analytical applications. The values of RSD below 5% suggests that the precision of the proposed method is reliable and it could be used for the detection of 2-chlorophenol in the real environment samples. The results indicated that the sensor is promising for real analytical measurements.

Table 4. 3 Application of g-C₃N₄/CDs/CGE sensor for the determination of 2-CP in effluent and tap water samples

Sample	Added (μM)	Found (μM)	Recovery/%(DPV)	RSD/%
Effluent water	3	2.81	93.7	2.61
	5	4.66	93.2	1.66
	7	7.34	104	2.97
Tap water	3	3.55	118	3.94
	5	5.61	112	3.95
	7	7.47	106	2.28

4.8 Sub-Conclusion

This work has shown that 2-chlorophenol can be detected by differential pulse voltammetry on a carbon dots-graphitic carbon nitride modified glassy carbon electrode. The nanocomposite as a modifier, enhanced the detection of 2-chlorophenol with a detection limit of 0.62 μM. The simple method was used for real water samples with satisfying percentage recoveries and relative standard deviation results. Thus the electrochemical sensor reported in this work could be used as an analytical tool.

CHAPTER 5

Electrochemical detection of arsenic (III) on a carbon dots-graphitic carbon nitride modified glassy carbon electrode

5.1 Optimisation of pH

The selection of optimum pH for arsenic detection was studied with DPV. The effect of pH was examined to determine the pH where As (III) is most available for the electrochemical detection using g-C₃N₄/CDs/CGE. Both pH 1 and pH 3 displayed wider and not well defined peaks despite having lower oxidation potential (0.48 and 0.54 V, respectively) compared to that of pH 6 (0.72 V). The highest peak current (13.8 μ A) was obtained at pH 6 and this was used as the working pH for arsenic sensing (**Figure 5.1**). The effect of pH on arsenic sensing was done because the ionic state of metals can be affected by the proton environment (pH).

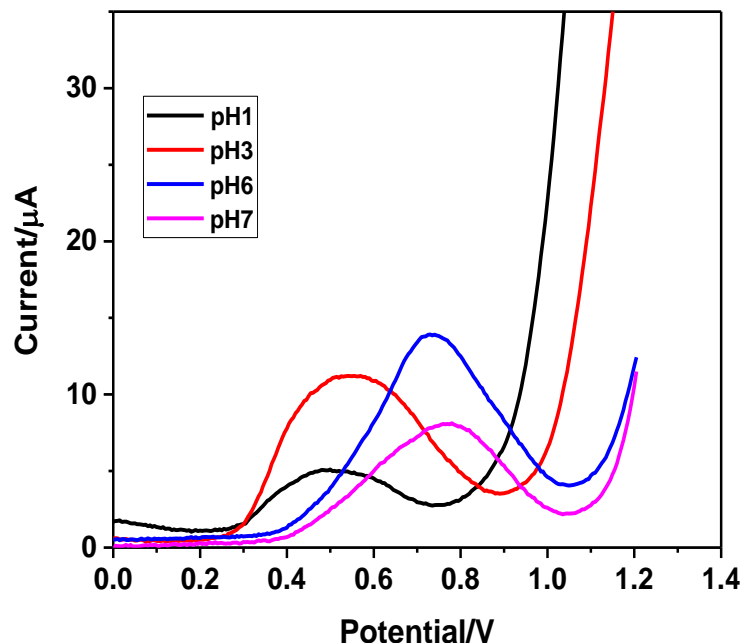


Figure 5. 1 DPV plots of 2 μM As (III) at g-C₃N₄/CDs/GCE in 0.1 M PBS at different pH values

5.2 Electrochemical detection of As (III)

5.2.1 DPV of the bare (GCE), g-C₃N₄/GCE, CDs/GCE and g-C₃N₄/CDs/GCE in 2 μM As (III)

The detection of As (III) was performed first with four different electrodes (GCE, g-C₃N₄/GCE, CDs/GCE and g-C₃N₄/CDs/GCE). As illustrated in **Figure 5.2**, the GCE electrode was not sensitive enough to detect As (III) ions as it showed the weakest peak intensity with a higher oxidation potential (1.67 μA , 0.87 V) compared to the g-C₃N₄/CDs/GCE electrode which displayed higher sensitivity with a higher peak intensity (26.45 μA). Hence, g-C₃N₄/CDs/GCE was used to record DPVs of different concentrations of As (III) and subsequently used to calculate the detection limit.

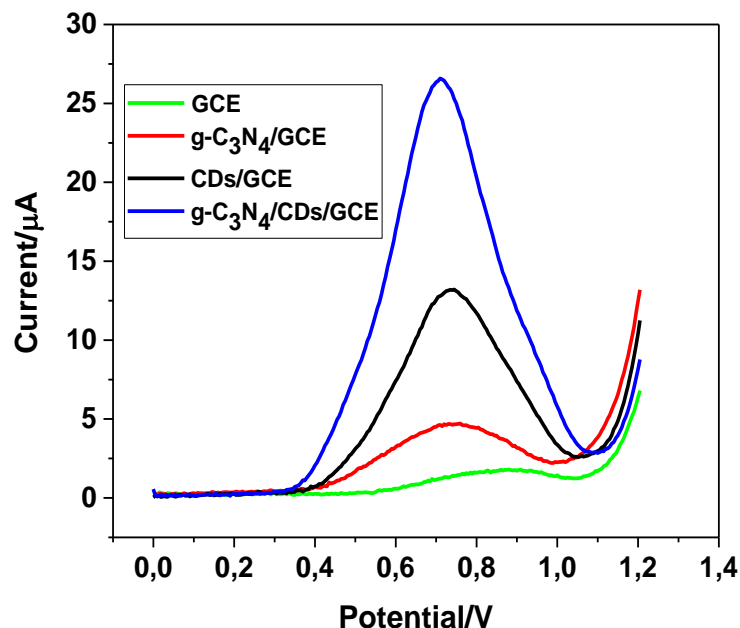


Figure 5. 2 DPV plots of GCE, g-C₃N₄/CGE, CDs/GCE and g-C₃N₄/CDs/CGE in 0.1 M PBS (pH = 6) containing 6 μM of As (III)

5.2.2 Electrochemical detection of As (III) at g-C₃N₄/CDs/CGE

The DPV plots of different As (III) concentrations between 2 μM to 10 μM were recorded using the optimized conditions. The peak currents increased linearly with arsenic concentration as shown in **Figure 5.3A**. The calibration graph is shown in **Figure 5.3B**. The linear regression equation for As (III) detection was $y = 2.2954x - 1.3313$, with $R^2=0.978$. The limit of detection was defined as: $LOD = 3\sigma/m$,

Where LOD, σ and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively. The limit of detection was calculated to be 1.64 μM or 123 ppb (123 μg/L).

The low detection limit obtained in this work can be attributed to the presence of CDs and g-C₃N₄ nanoparticles which greatly enhanced the As (III) ion signal by increasing the surface area and conductivity of the glassy carbon electrode. In **Table 5.1**, the performances of different fabricated

electrodes towards arsenic electro-oxidation are compared. The sensor based on the g-C₃N₄/CDs/CGE is not the most sensitive electrode but it exhibits considerably high performance.

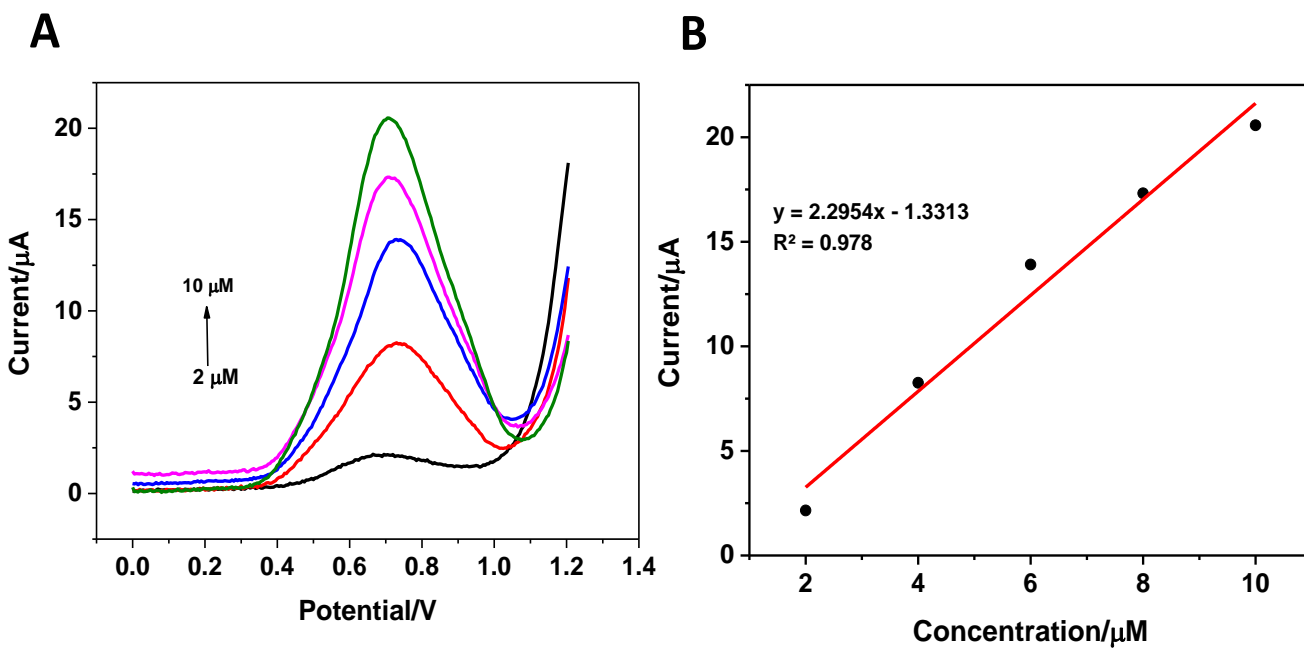


Figure 5. 3 (A) DPV plots of various concentrations of As (III) (2-10 μM) at g-C₃N₄/CDs/GCE in 0.1 M PBS (pH = 6), (B) The linear relationship between oxidation peak current and the concentration of As (III)

Table 5. 1 Comparative study on the performance of different electrochemical sensors for As (III) detection

Sensors	Linear range (μM)	Limit of Detection (μM)	pH	Oxidation potential (V)	References
SrTiO ₃ /β-CD/GCE	10-140	0.02	7	0.16	(Karthika et al., 2019)
ERGO-AuNPS/GCE	0.01-5	0.002	7	0.1	(Liu et al., 2013)
Pt/Fe(III)MWCNT/GCE	0-10	0.01	-	0.82	(Shin and Hong, 2010)
AuNPS/GCE	280-14×10 ⁵	0.004	1	0.1	(Idris et al., 2017)
AuCNTS/GCE	-	0.001	-	0.2	(Xiao et al., 2008)
CoO/GCE	10-300	0.01	7	0.75	(Abdollah Salimi et al., 2008)
g-C₃N₄/CDs/GCE	2-10	1.64	6	0.72	This work

5.3 Reproducibility of g-C₃N₄/CDs/GCE sensor

The reproducibility of g-C₃N₄/CDs/GCE electrode was estimated by recording the responses of 2 μ M of As (III) in 5 different DPV measurements (**Figure 5.4**) and the RSD was calculated to be 7.5%, implying good reproducibility of the fabricated sensor.

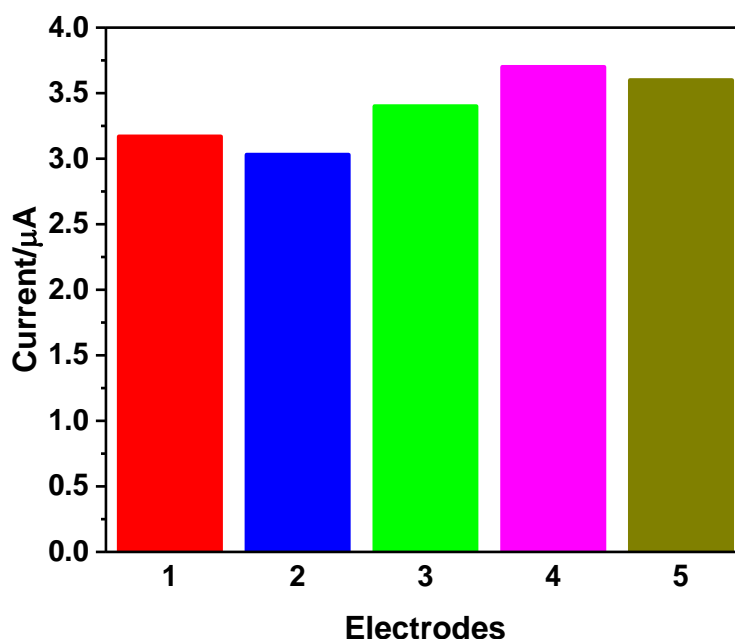


Figure 5. 4 Reproducibility of g-C₃N₄/CDs/CGE modified electrode with 5 different DPV response measurements for 2 μ M As (III) in 0.01 M PBS at pH 6

5.4 Stability of g-C₃N₄/CDs/GCE sensor

To measure its stability, g-C₃N₄/CDs/CGE was stored at 4°C for 15 days and the current response of 4 μ M of As (III) was measured each three day. Notably, the stability of the electrode toward arsenic determination showed a decreased peak intensity over the 15 days, which could be explained by the dissolution of the nanocomposite into the electrolyte solution or by surface passivation of the nanocomposite after multiple runs (Zerdoumi et al., 2019).

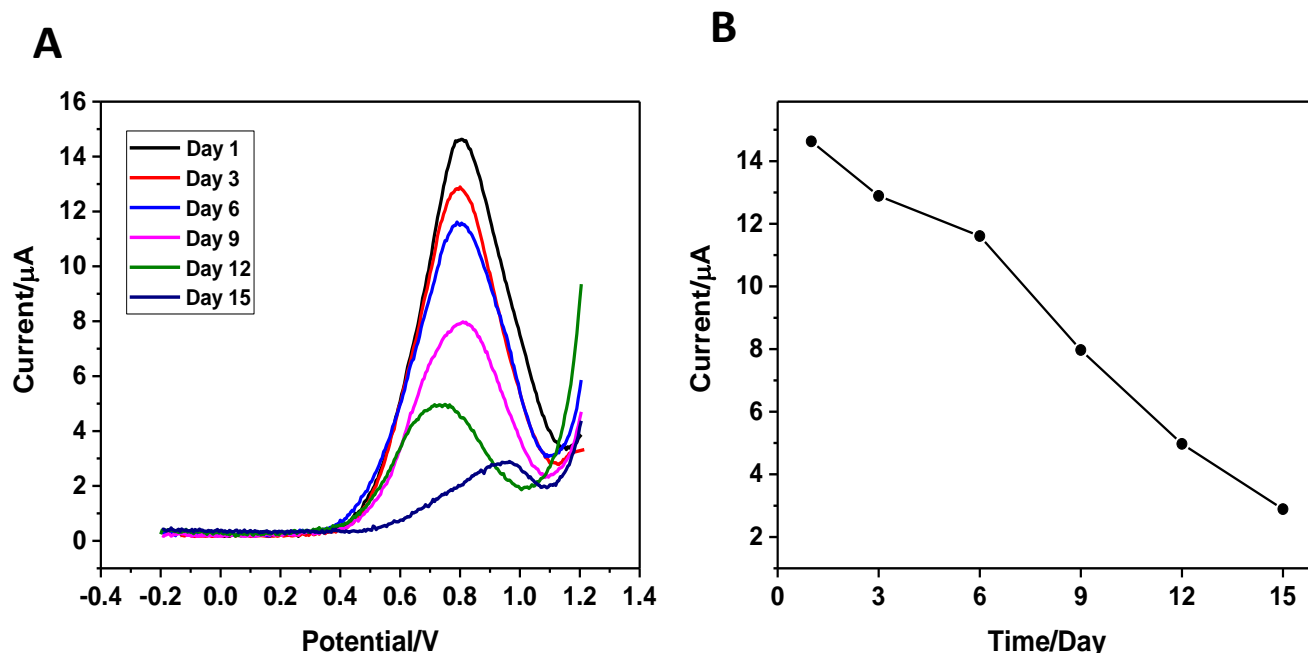


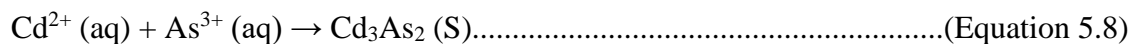
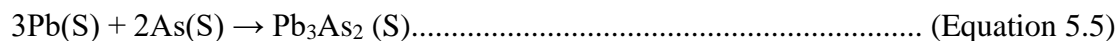
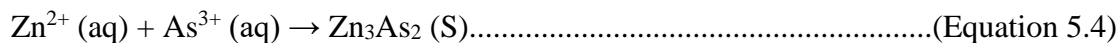
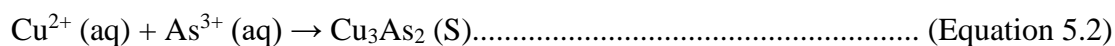
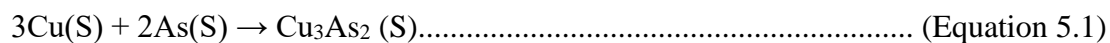
Figure 5. 5 (A) Stability of g-C₃N₄/CDs/CGE modified electrode with repetitive measurements of DPV response over two weeks for 4 μM As (III) in 0.01 M PBS at pH 6, (B) Relationship between current and time

5.5 Interference studies

The drawback of As (III) detection using DPV is that, it is susceptible to interferences by various cations which are oxidized at a similar potential to As (III) and this can cause an increase or a decrease in the peak current of the arsenic signal (Olayiwola, 2016). Copper has been found to be the most significant interference cation in arsenic sensing among other ions such as cadmium, manganese, iron, zinc and lead (Tiwari and Lee, 2017, Zhou et al., 2017, Olayiwola, 2016). It has also been documented in the literature that copper was able to form an intermetallic compound with arsenic in solution, which results in an increase in peak current signal (Piech and Kubiak, 2007). The interference from various ions during As(III) determination can be overcome by masking with EDTA, which forms chelating complexes with the interfering ions, making them bulky enough (Kempahanumakkagari et al., 2017).

Interference caused by other inorganic metal ions was investigated to test the selectivity of modified electrode toward As (III) detection.

The g-C₃N₄/CDs/CGE was found to be susceptible to interferences from Pb²⁺, Cu²⁺, Cd²⁺ and Zn²⁺ with an increase in peak current of 22%, 45%, 47% and 53%, respectively (**Figure 5.6A**). This increase in peak intensity can be due to the proximity of the oxidation potential of those metal ions with arsenic and also the formation of intermetallic bonding between interfering ions and arsenic as depicted in the following equations:



The interference from various ions during As (III) determination can be overcome by masking with EDTA. When equal concentrations of EDTA was added to the arsenic, the interfering ions decreased the peak intensity for all interfering ions (27%, 29%, 30%, and 76% decrease) for Pb²⁺, Zn²⁺, Cd²⁺ and Cu²⁺, respectively (**Figure 5.6B**). This may be due to the formation of chelating complexes (see equations below) between EDTA and the interfering ions, making them bulky enough, thus allowing only arsenic detection. EDTA prevented inter-metallic bonding between the interfering ions and arsenic thus increased the selectivity of the fabricated sensor;

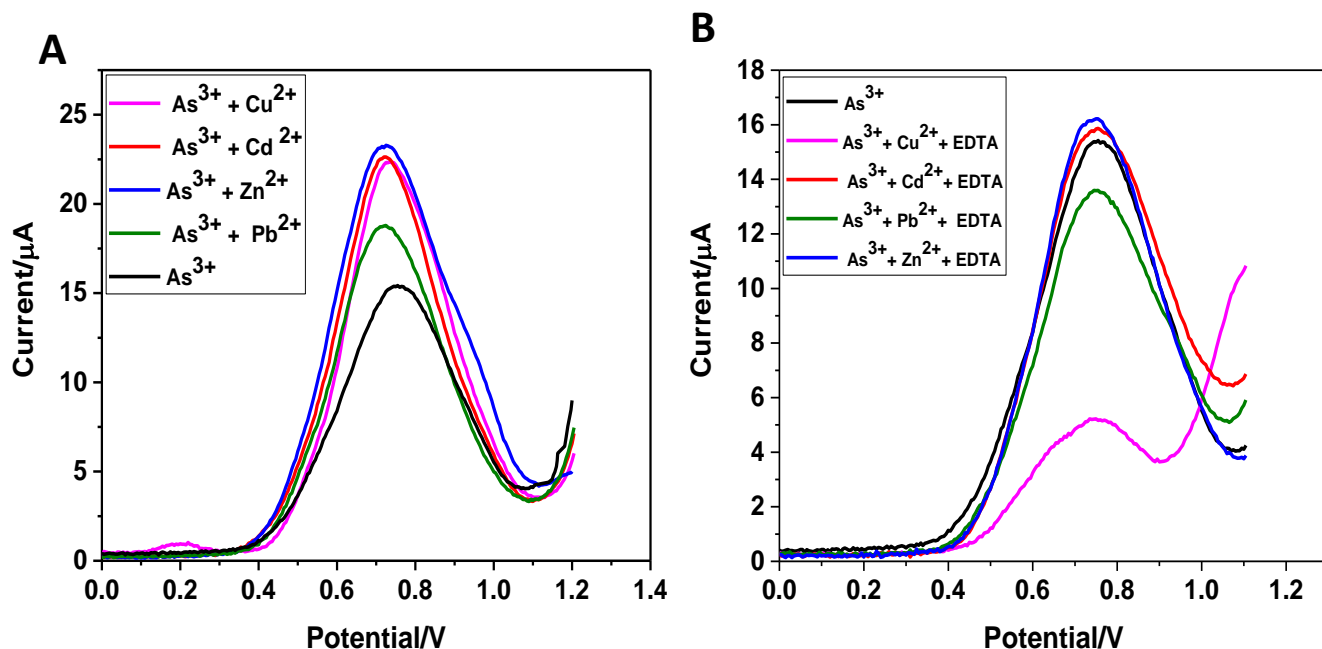
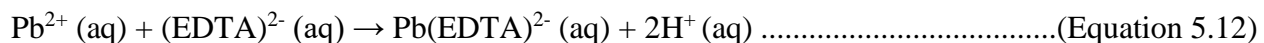
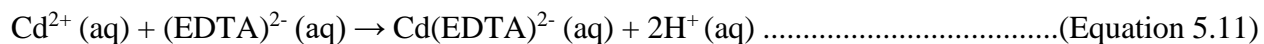
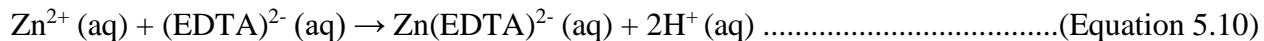
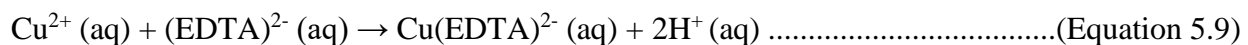


Figure 5. 6 DPV plots of 2 μM As (III) (A) with 2 μM of different interfering ions (B) with different interfering ions + 2 mM EDTA

5.6 Arsenic detection in Water samples

In order to evaluate the practical application of g-C₃N₄/CDs/CGE as an arsenic sensor, arsenic detection was performed in tap and effluent water samples by the DPV method. The standard addition method was used for the determination of arsenic. The preparation of water samples and electrolyte solution were done as stated in an earlier section (**Section 4.7**), with an optimum pH of 6. Different amounts of As (III), were added into the water samples to test recovery rates. The results shown in **Table 5.2** indicated that the recovery rates of arsenic were 94 to 98% and 86 to 100% in tap and effluent water samples, respectively. The satisfactory recovery values obtained with g-C₃N₄/CDs/CGE confirmed good accuracy of the reported sensor and its applicability to the real life sample analysis.

Table 5. 2 Application of g-C₃N₄/CDs/CGE sensor for the determination of As (III) in effluent and tap water samples

Sample	Added (μM)	Found (μM)	Recovery/%(DPV)	RSD/%
Effluent water	3	2.93	98	1.35
	5	4.93	99	4.31
	7	6.54	94	4.06
Tap water	3	2.57	86	3.79
	5	5	100	2.91
	7	6.68	95	3.34

5.7 Sub-Conclusion

A simple, reproducible and fast method of detecting As (III) in water was developed by modifying glassy carbon electrode with CDs and g-C₃N₄. The modified electrode was used to sense the analyte using differential pulse voltammetry, and a detection limit of 1.64 μM was obtained. This demonstrates that the sensor has analytical significance. The applicability of the proposed modified electrode was highlighted by its application for real water analysis. The results obtained from the percentage recovery were within the acceptable range thus showing reliability of the sensor for arsenic detection.

CHAPTER 6

Electrochemical detection of sulfamethoxazole on carbon dots-graphitic carbon nitride modified glassy carbon electrode

6.1 Effect of pH

The effect of pH on the anodic peak current of SMX at the g-C₃N₄/CDs/CGE modified GCE was investigated by DPV (see **Figure 6.1**). The pH range studied was from 4–7. A well-defined oxidation peak and a high peak current were obtained at pH 5. So pH 5 was selected as the optimal pH.

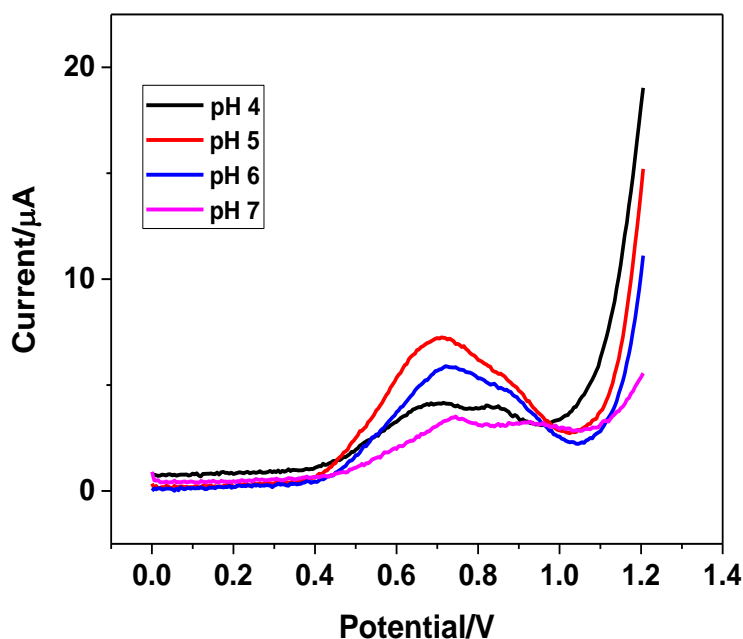


Figure 6. 1 Effect of pH on the anodic current of 0.5 μ M SMX at g-C₃N₄/CDs/GCE in 0.1M PBS

6.2 Electrochemical behaviour of SMX at different electrodes

The electrochemical behaviour of SMX at bare GCE, g-C₃N₄/GCE, CDs/GCE and g-C₃N₄/CDs/GCE modified GCE was studied by DPV. The bare electrode sensitivity to SMX oxidation was poor, as no oxidation peak was observed. Sulfamethoxazole gave a well-defined higher oxidation peak at 0.65 V with a peak current of 17.8 μ A at g-C₃N₄/CDs/GCE compare to the other electrodes (g-C₃N₄/GCE and CDs/GCE). Those oxidation peaks of SMX might arise due to the oxidation of the electrochemically active amino group on SMX, (Issac and Girish Kumar, 2009), (see **Figure 6.2**). The oxidation peak current of SMX has greatly increased at the g-C₃N₄/GCE. Thus, by modifying GCE with CDs/g-C₃N₄, the electrode reactivity was found to be greatly increased as indicated by the enhancement in peak current. The remarkable peak current enhancement, proved the electrocatalytic activity of g-C₃N₄/GCE in the oxidation of SMX. This may be attributed to the increase in the effective surface area of GCE when modified with g-C₃N₄/CDs.

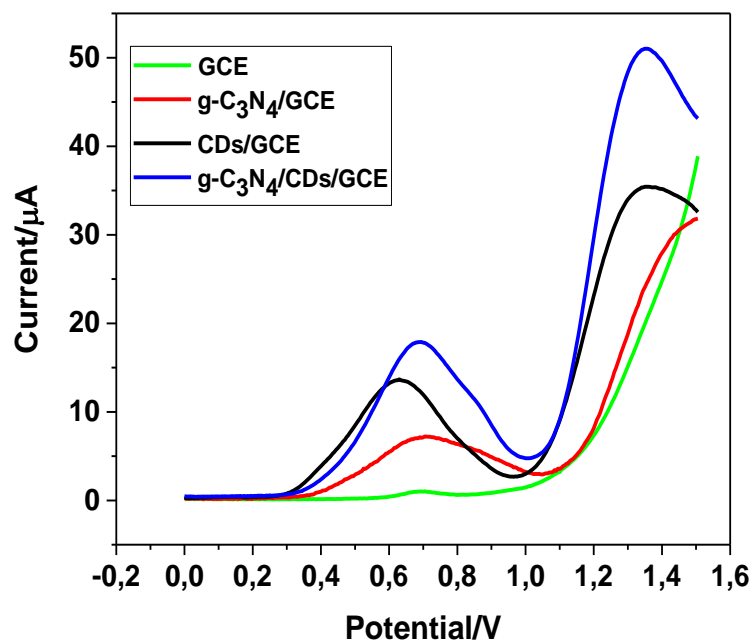


Figure 6. 2 DPV plots of GCE, g-C₃N₄/CGE, CDs/GCE and g-C₃N₄/CDs/CGE in 0.1 M PBS (pH = 5) containing 0.7 μ M SMX

6.3 Effect of the amount of g-C₃N₄/CDs dispersion

The effect of the amount of g-C₃N₄/CDs dispersion on the anodic peak current of SMX was evaluated (see **Figure 6.3**). As the amount of g-C₃N₄/CDs dispersion was increased from 6 μ L up to 12 μ L, the oxidation peak current was greatly enhanced. The enhancement of the current indicates that the specific surface area and the number of catalytic sites increase with an increase of g-C₃N₄/CDs amount. When the amount of g-C₃N₄/CDs dispersion was more than 12 μ L, the oxidation peak current decreased slightly. This indicates that the excess of g-C₃N₄/CDs blocks the electron transfer of SMX (Issac and Kumar, 2009). So the amount of g-C₃N₄/CDs dispersion was fixed at 12 μ L.

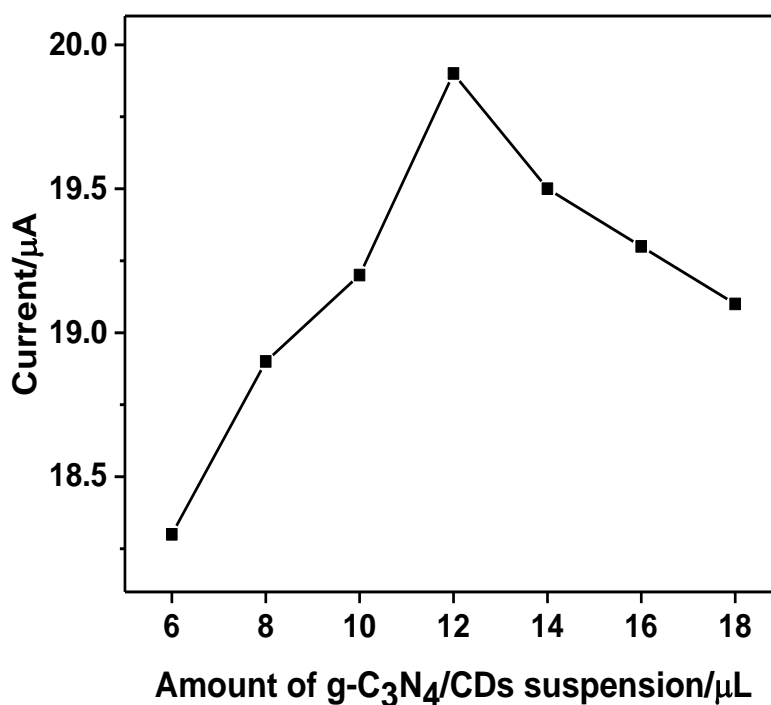


Figure 6. 3 Effect of the amount of 0.9 μ M g-C₃N₄/CDs suspension

6.4 Electrochemical detection of SMX

The performance of g-C₃N₄/CDs/CGE for the determination of SMX in 0.1 mol/L PBS (pH 5.0) was further evaluated with different concentrations from 0.3 to 1.1 μ M, under optimized experimental conditions. As shown in **Figure 6.4**, when the concentrations of SMX was increased, the DPV oxidation peak currents increased proportionally with the concentrations and the oxidation peak potentials almost kept unchanged. A linear response segment of SMX was obtained, which was expressed as $I_{pa} (\mu A) = 15.771 C_{SMX} (\mu mol/L) + 2.6041$ ($R^2 = 0.9906$). The detection limits was calculated to be 0.10 μ M. This results indicated that g-C₃N₄/CDs/CGE could be applied for the detection and quantification of SMX.

The LOD values and linear ranges for SMX detection were compared with those from previous work performed with different electrode materials, summarized in **Table 6.1**. It is worth mentioning that g-C₃N₄/CDs/CGE modified electrode exhibits satisfactory performance with a high sensitivity and was among the electrodes displaying lower LOD (0.10 μ M) when compared with those from previous works. The good electrode performance could result from the high surface area of the g-C₃N₄/CDs nanocomposite, leading to an increase of electrochemical active sites which enhanced its sensitivity toward SMX analyte.

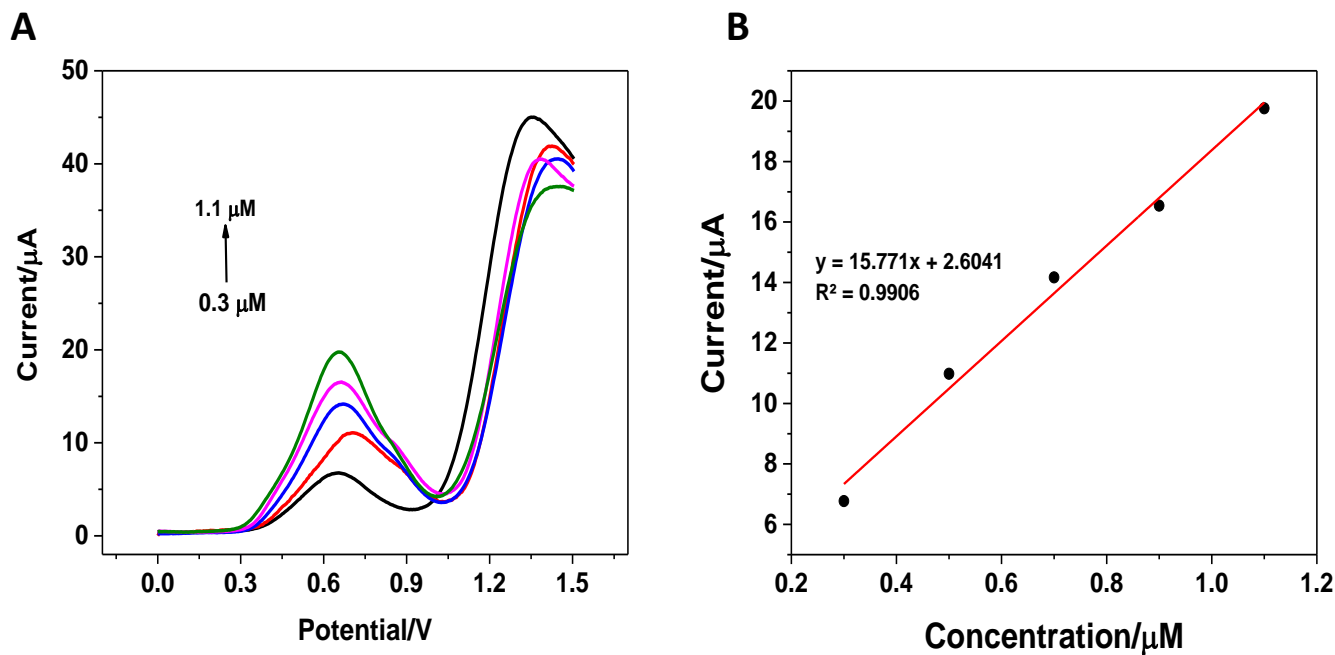


Figure 6. 4 (A) DPV plots of various concentrations of SMX (0.3-1.1 μM) at g-C₃N₄/CDs/GCE in 0.1 M PBS (pH = 5), (B) The linear relationship between oxidation peak current and the concentration of SMX

Table 6. 1 Comparison of different chemically modified electrodes for determination SMX

Sensors	Linear range (μM)	Limit of Detection (μM)	pH	Oxidation potential (V)	References
MoO ₂ /GCE	10-100	0.144	7	0.85	(Khanfar et al., 2020)
Ag ₂ /MWCNTs/GCE	2.10 ⁻⁵ -0.1	4.06 \times 10 ⁻⁶	7.4	0.2	(Zhang, 2020)
1M3OIMZTFB/NiO-NPs/CPE	0.003-400	0.001	7	0.9	(Salmanpour, 2019)
MWCNT/PBnc/SPE	1-10	0.038	7	0.65	(Sgobbi et al., 2016)
MIP/GCE	0.2-1.4	0.05	-	0.2	(Zhang, 2019)
TYR/SPCE	20-200	22	8	0.5	(Del Torno-de Román et al., 2016)
g-C₃N₄/CDs/GCE	0.3-1.3	0.10	5	0.65	This work

6.5 Reproducibility and stability

The reproducibility of the sensor was examined by measuring the current response of SMX oxidation at five equally fabricated electrodes under the same conditions (**Figure 6.5A**). The relative standard deviation of the current response was 6.1 % indicating that the reproducibility of the sensor was accurate.

The prepared g-C₃N₄/CDs/CGE was stored in a refrigerator at 4°C for 15 days, the stability of g-C₃N₄/CDs/CGE has been evaluated for 15 days in 0.1 mol/L PBS (pH 5.0). The peak current decreased by 80%, indicating that the stability of the g-C₃N₄/CDs/CGE was not good enough (**Figure 6.5B**).

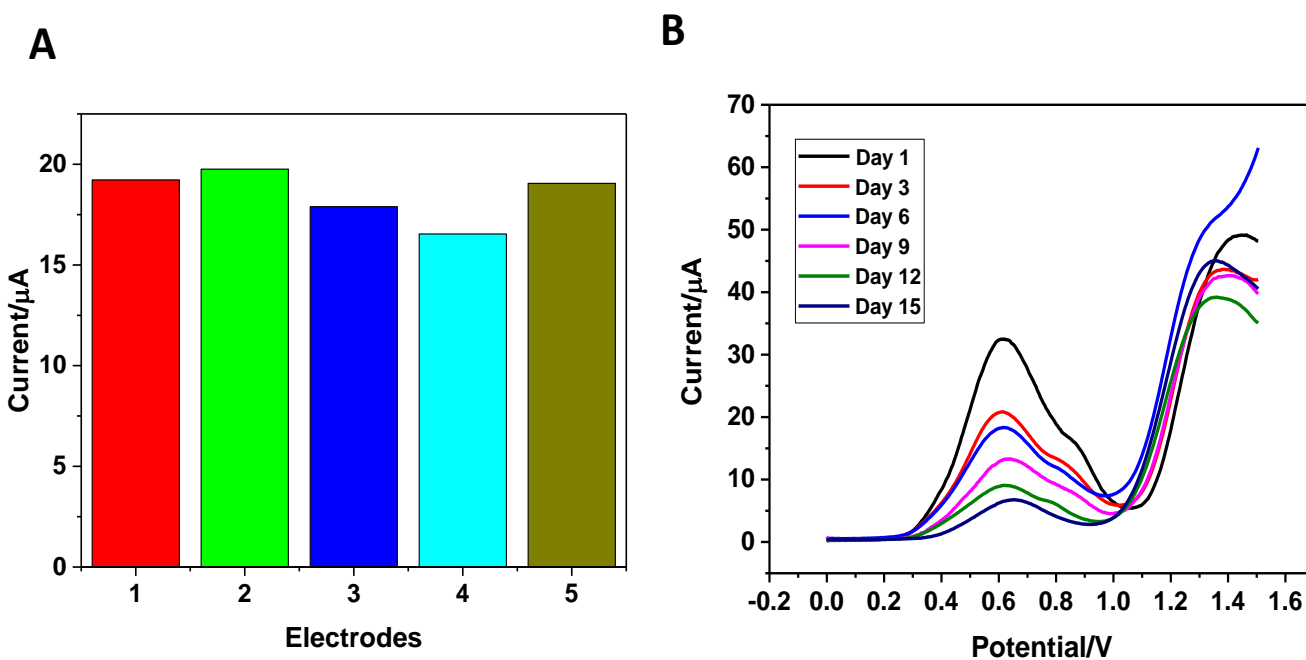


Figure 6. 5 (A) Reproducibility of g-C₃N₄/CDs/CGE modified electrode with 5 different DPV response measurements for 0.5 μM SMX in 0.01 M PBS at pH 5 (B) Stability of g-C₃N₄/CDs/CGE modified electrode with repetitive DPV measurements over two weeks for 1.1 μM SMX in 0.01 M PBS at pH 5

6.6 Water samples analysis

The proposed electrochemical method for the determination of SMX was applied to water samples (pH of 8.01 and 7.77 for effluent sample and tap water respectively, were adjusted to optimum pH 5). The recoveries from tap and effluent water were measured by spiking water samples with known amounts of SMX antibiotics (0.4, 0.6 and 0.8 μM) then diluting the samples in PBS pH 5 (**Figure 6.6**). The results are shown in **Table 6.2** and the recoveries obtained are in the range of 88–105% while the relative standard deviation (RSD) is under 6%. The good recovery indicating that the proposed sensor was reliable for the determination of sulfamethoxazole in real samples.

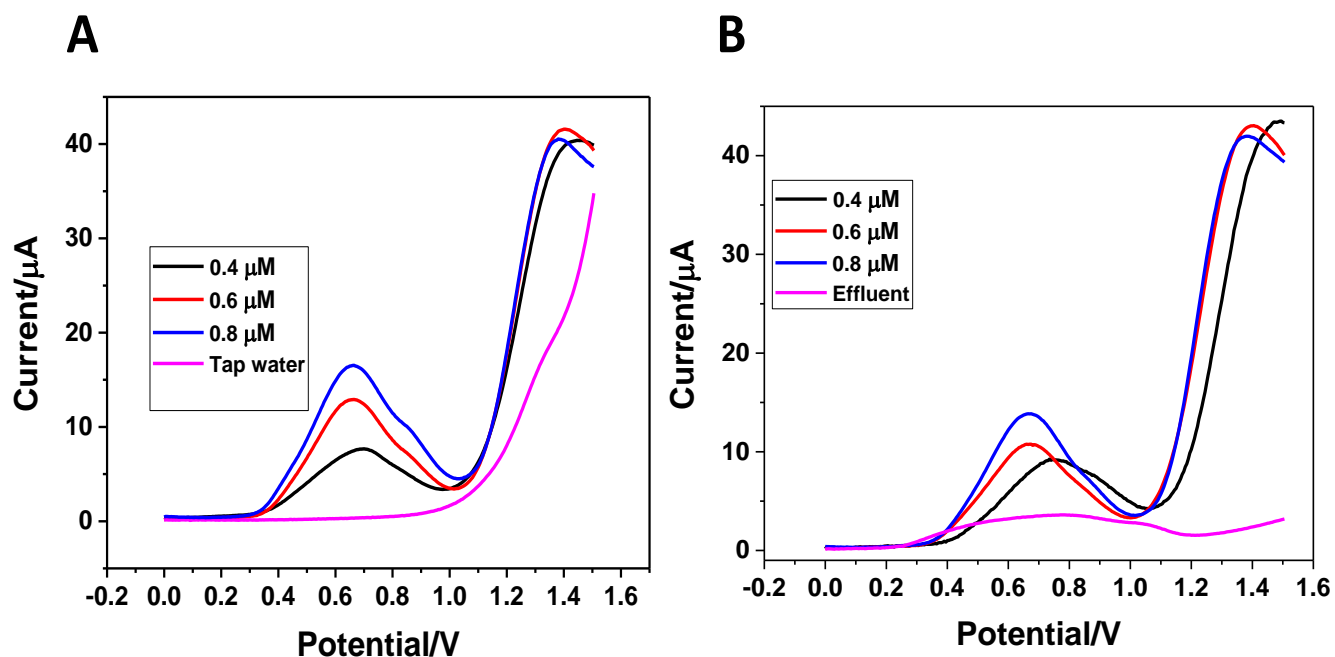


Figure 6. 6 DPV plots of SMX detection in real water samples (A) Tap water (B) Effluent

Table 6. 2 Application of g-C₃N₄/CDs/CGE sensor for the detection of SMX in effluent and tap water samples

Sample	Added (μM)	Found (μM)	Recovery/%(DPV)	RSD/%
Effluent water	0.4	0.42	105	3.71
	0.6	0.52	87	4.56
	0.8	0.71	89	2.76
Tap water	0.4	0.32	80	5.87
	0.6	0.65	108	4.58
	0.8	0.70	88	2.45

6.7 Co-detection of 2-CP, As (III) and SMX

The proposed sensor g-C₃N₄/CDs/CGE has been tested for the simultaneous determination of 2-CP, SMX and As (III) in water using DPV. **Figure 6.6** shows the DPV responses for 2-CP, SMX and As (III) with equal concentration (2 μM) at neutral pH 7. A well-defined oxidation peak at 0.44 V, corresponding to the oxidation peak of 2-chlorophenol can be observed. Two other small ill-defined peaks can be observed at 0.73 V and 0.93 V and can be attributed to the oxidation peak of sulfamethoxazole and arsenic, respectively. The lack of pronounced oxidation peaks for SMX and As (III) analytes could be explained by the electrode being more sensitive to 2-CP than the two other analytes. Furthermore, the optimum pH for sulfamethoxazole and arsenic oxidation was set at pH 5 and 6, respectively, based on this present study. More pronounced peaks may be obtained if the concentrations of As (III) and SMX are increased. The results indicated that g-

C₃N₄/CDs/CGE can be an appropriate platform for the simultaneous determination 2-CP, SMX and As (III).

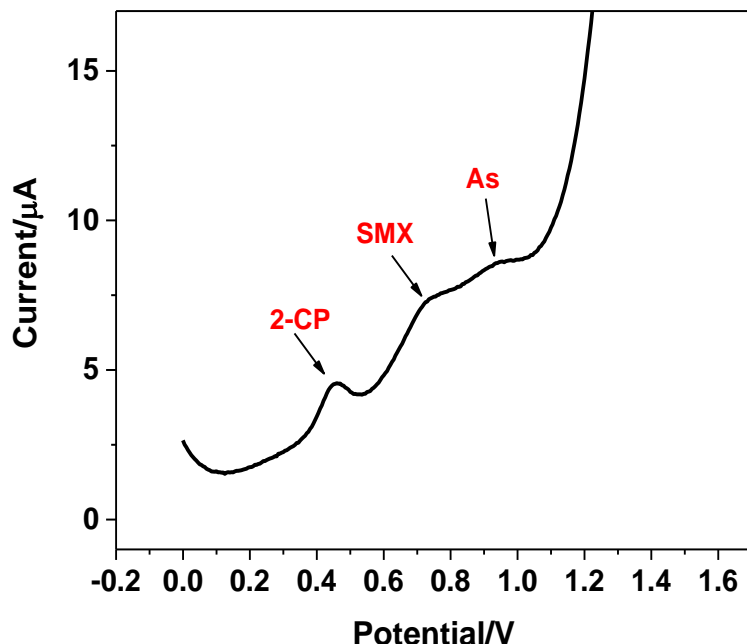


Figure 6. 7 Simultaneous DPV detection at g-C₃N₄/CDs/CGE in 0.1M PBS (PH 7.0), containing equivalent concentration (2 μ M) of 2-CP, SMX and As (III)

6.8 Sub-Conclusion

Voltammetric determination of SMX at a g-C₃N₄/CDs/GCE was investigated by DPV. Carbon dots and graphitic carbon nitride showed electrocatalytic action for the oxidation of SMX, characterized by the enhancement of the peak current, lower detection limit and a reduction of peak potential compared to other previously reported electrodes. This was probably due to the larger effective surface area of the nanocomposite and an increase in the number of reaction sites. The g-C₃N₄/CDs/CGE provided a good platform for the determination of SMX in tap and effluent water samples.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusion

In this work, a nanocomposite of carbon dots (CDs) and graphitic carbon nitride (g-C₃N₄) was prepared, characterized and used as an electrode modifier to fabricate an electrochemical sensor. The successfully fabricated electrochemical sensor (g-C₃N₄/CDs/GCE) was used for the determination of arsenic (III), 2-chlorophenol and sulfamethoxazole in water. The synergy between g-C₃N₄ and CDs resulted in the nanocomposite displaying high electron transfer, greater electroactive surface area and hence, improved sensitivity toward the analytes. The electrochemical sensor was used under optimal conditions for the detection of arsenic (III), 2-chlorophenol and sulfamethoxazole. Lower detection limits values for the three analytes were obtained (0.62, 1.64 and 0.10 μ M for 2-CP, As (III) and SMX, respectively). The nanocomposite exhibited notable current enhancement and good sensitivity in the determination of 2-chlorophenol, arsenic and sulfamethoxazole. However, the stability of the electrode was not as good as expected. The sensor was used successfully for the practical analysis of arsenic, 2-CP and SMX in water samples. The recovery percentages for the detection of known analyte concentrations in water samples were within the acceptable range (80-120%), confirming the reliability and analytical performance of the sensor. This research provided an easy and sensitive tool for the comprehensive monitoring of arsenic, 2-CP and SMX in water.

7.2 Recommendations

The following recommendations are made for possible future investigations.

- The versatility of the modified electrode used as sensor in this work can be further studied by applying it to different water samples from different environment or different pollution loads.
- The stability of the fabricated electrode was poor and the oxidation current gradually decreased with successive measurements. One reason for this may be that the g-C₃N₄/CDs nanocomposite was easily dispersed into the reaction solution. To protect against the loss of the nanocomposite, an electrode fixative can be used. Among many fixatives, the following can be used: Polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), Nafion or Chitosan (CS).
- The effect of mass ratio of the synthesized nanomaterials (g-C₃N₄ and CDs) on the sensitivity of the modified electrode can also be studied for optimization of detection.

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