UNIVERSITY OF NAIROBI

ELECTROCATALYTIC DECOMPOSITION OF TETRACHLORVINPHOS IN ACETONITRILE-WATER MEDIA USING CYANOCOBALAMIN

BY

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DECLARATION

I declare that this Thesis is my original work and has not been submitted elsewhere for research. This has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements, in places where other people's work or my work has been used.

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ABSTRACT

This study investigated the electrocatalytic degradation of tetrachlorvinphos pesticide standard in acetonitrile-water media using cyanocobalamin catalyst. It was initiated by reports recorded from various consumers who link their ailment with possibility of pesticide residues in both *flora and fauna*. Although some studies have been done on electrochemical behavior and rate of degradation of pesticides, no detailed data is available on the same for tetrachlorvinphos pesticide. The study was carried out using cyclic voltammetry and UV-Vis spectrophotometry at a temperature of 24 ± 1 ˚C. The working electrode potential was concurrently recorded for the resulting current. A preliminary study for cyclic voltammetry was done using a well-known redox couple (Potassium ferricyanide) in order to calibrate the instrument and validate the results. The resulting voltammograms data were analyzed for fundamental information regarding the redox reactions. For UV-Vis spectrophotometry, absorbance values for substrate were recorded at the maximum absorption wavelengths for various concentrations. The data obtained were, analyzed and interpreted using Kaleidagraph software, version 4.1.1 and Microsoft Excel 2010 statistics software. The result shows that tetrachlorvinphos pesticide availed a two consecutive one-electron reduction peaks; the first (not well-defined) reduction peak at $\sim - 0.710 \pm 0.004$ V and a second (well defined) reduction peak $\sim -1.096 \pm 0.029$ V Versus Ag/AgCl. The diffusion coefficient was reported as $3.68 \times 10\text{-}5 \text{cm}^2\text{s}^{-1}$. The current density was 5.83×10^{-5} A/cm^2. The reduction potential for Tetrachlorvinphos pesticide in the presence of cyanocobalamin catalyst using a glassy carbon electrode was $- 0.923 \pm 0.03$ V versus Ag/AgCl with a diffusion coefficient was 3.37×10^{-5} cm^{2}s^{-1}. The current density was 2.56×10^{-5} A/cm^2. The value for reduction potential of Tetrachlorvinphos pesticide in the two cases resulted to lowering of over-potential by 0.168 V implying energy saving. The UV-Vis Spectrophotometer recorded maximum absorption wavelength of Tetrachlorvinphos alone at 250 nm and with a catalyst at (340.0, 400.0 and 540.0) nm respectively. This shows that, electrocatalytic reduction of tetrachlorvinphos pesticide occurred at a significantly lower potential compared to direct reduction with an energy saving of 0.168 V. Cyanocobalamin is a possible suitable catalyst for the degradation of tetrachlorvinphos.

DEDICATION

This work is dedicated to my dear wife Esther, whose love and support has been pivotal during my academic journey; to my daughter Milka whose social lives were disrupted during this period; and to my parents Mr. & Mrs. Nkunu who brought me to this world.

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LIST OF ABREVIATIONS AND ACRONYMS

Ag/AgCl	Silver-Silver Chloride
AcHE	Acetocholinesterase Enzyme
C-C	Carbon-Carbon bond
C-O	Carbon-Oxygen bond
DDT	Dichloro-diphenyl-trichloroethane
EDA	Ethyl di-acetate
EP	Extreme Pressure
E_{pa}	Anodic peak potential
E_{pc}	Cathodic electrode potential
$E^{0'}$	Formal electrode potential
FAO	Food Agriculture organization
HOMO	High occupied molecular orbital
IUPAC	International Union of Pure and Applied chemistry
i_{pa}	Peak anodic current
i_{pc}	Cathodic peak current
KEBS	Kenya Bureau of Standards
LUMO	Low unoccupied molecular orbital
nm	Nanometers
pH	Hydrogen Potential
SCE	Saturated Calomel Electrode
U.S. EPA	United States Environmental Protection Agency
Vitamin B_{12}	Cyanocobalamin

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CHAPTER ONE

INTRODUCTION

1.1. Background

The use of pesticides has greatly increased food production, which is urgently needed by the ever increasing population (FAO, 2011). However, the occurrence of a number of pesticide residues in the environment and in the food cycle is causing anxiety (Brown, 2004). Because most of the man-made pesticides such as organophosphates compounds linger in the environment, intractable towards decomposition, they bio-accumulate in the food chain, and thus impact the ecosystem negatively for longer period of time (Ayas *et al.,* 1997).

In many Sub-Sahara Africa counties like Kenya, tetrachlorvinphos pesticide is one of the most commonly used contact insecticides against most storage pests like weevils, rodents and fungi (Obeng-Ofori *et al,* 2015). In cases where resistance is conjectured, higher doses are applied to increase efficiency, hence leading to rise in the residue levels in the stored products. tetrachlorvinphos pesticide is also used in Kenya in many formulations of pet flea collars, sprays and shampoos for the treatment and control of ecto-parasites in pet animals like cats, dogs and horses (EPA, 2002).

During the application of tetrachlorvinphos pesticide, it may be absorbed through the skin and pose a health risk workers who apply and other people who may interact with the treated animals. Studies done in Canada revealed that, a prolonged exposure may lead to prostate and skin cancer in men (Guyton, 2015). Just like many organochlorine compounds (Aktar, 2009), tetrachlorvinphos pesticides residues are also detrimental to the unprotected (Kim *et al,* 2017) because of their persistence and recalcitrance towards degradation which leads to their accumulation in the food chain. There are studies by Ortiz-Hernández & Sánchez-Salinas, (2010) shows degradation

metabolites of tetrachlorvinphos pesticide by bacteria strain *Serratia ficaria* in Mineral Medium (MM) and Trips casein soy agar (TS) through hydrolysis producing 1- (2,3,4) trichlorphenylethanone and 1-(2,4,5) trichlorophenyl-ethanone less toxic than parent molecule. Photo degradation is also another abiotic process that uses the solar energy to degrade a pesticide. This abiotic and biotic degradation pathway available is inadequate and therefore calls for an additional alternative method.

As a consequence, it is our obligation to monitor the degree and extent of environmental contamination by these compounds. When in the environment, some of these chemicals can undergo abiotic hydrolysis, photo-degradation and biodegradation (Fenner *et al.*, 2013). There are several existing techniques for removing harmful chemicals from chlorinated hydrocarbon compounds in the environment. Among the detoxification artistry, electrochemical reduction is an appropriate alternative (Wanjau *et al*., 2015). The technique that is simple to operate, saves energy, and also produces much less poisonous products compared to other methods (Jalil *et al.*, 2007). The current study involved use of cyanocobalamin as a catalyst in the reduction of tetrachlorvinphos.

1.2. Pesticides

According to Ware (1983), a pesticide is a chemical compound used for preventing, destroying, repelling or abate any pest, (including weeds). It may be a chemical substance, bio-agent (such as bacteria, fungi, viruses, other microorganisms and their associated toxins), antimicrobial, disinfectant or contraption used against any pest (Deshayes *et al*., 2017). A Pest is a living organism (animal, plant or fungus) that damage property, transmit disease or are a carrier of disease or cause annoyance (Orerke, 2006). The use of pesticides results in improved quality and quantity in crop and animal yields. However, pesticide use kills soil microorganisms that affect soil fertility, contaminate groundwater and may trigger off immune-toxicity in humans and animals.

(Inserted Paragraph 2)

Some Organochlorine and Organophosphate compounds lead to immunotoxicity, suppresses immunity, causes allergies and inflammation of the body tissues (Thomas, 1995). Pesticides are classified according to the type of pest they control. These include: defoliants, desiccants, nematocides, avicides, herbicides, and rodenticides among others. Some synthetic Organohalide chemicals such as dichloro-diphenyl-trichloroethane (DDT) take many months or years (half-live of about 7 years) before degrading (Longnecker *et al.*, 1997). When DDT bio-accumulate in the food chain, it may cause pancreatic cancer, neurological disorders and non-hodgkin's lymphoma disease. The overwhelming evidence of the harm led to the ban of pesticide in many western countries including sub-Saharan African countries (Longnecker *et al.*, 1997).

1.2.1. Classification of pesticides

Major classifications includes: Organophosphates, Carbamates, Organochlorine, Pyrethroid, and Sulfonylurea among others. They have an effect on the impulse transmission in the central nervous system leading to sensory and behavioral disturbances such as sleep/wake, locomotor control and postural stability (Mesulam, 1995). The urea and thio-urea pesticides stop plants growth by inhibiting the action of plant enzymes controlling growth.

1.2.1.1. Organophosphate

Any group of organic chemicals containing phosphorous is known as organophosphorous compound (Marrs., 2001). Many of the organophosphate compounds with both industrial and environmental applications have phosphorous pentavalent predominant. They find wide range applications in the world as insecticides (Gunnell *et al.,* 2007). Their toxicity depends on the nature of substituents attached to phosphorus. Some common examples include Malathion, parathion, diazinon, fenthion, dichlorvos, chlorpyrifos, ethion, and Tetrachlorvinphos.

1.2.1.2. Carbamate Pesticides

Carbamates are derivatives of carbamic acid. Carbamate insecticides poison targets by irreversibly inactivating the enzyme acetylcholinesterase (Colović, 2013) which regulates acetylcholine. These pesticide residues in the environment degrade within weeks or months (Goel & Aggarwal, 2007). The common group of pesticides is carbaryl (Sevin), methomyl, aldicarb and carbofuran (Furadin). They are applied in granule and wettable formulations.

1.2.1.3. Organochlorine

A group of chlorinated compounds are also known as Organochlorine compounds. Their toxicity properties make them have wide applications in the chemical industry and agriculture. They are highly persist in the environment and thus banned in many developed countries (Aktar *et al.,* 2009). Organochlorine insecticides such as DDT, Chlordane, and toxaphene were banned in 1986 (Appendix A) from the market by Pesticide Control Products Board of Kenya due to their health and environmental effects. These hydrocarbon derivative compounds are highly toxic and slow to degradation.

1.2.1.4. Pyrethroids

Pyrethroids are artificial pesticides such as permethrin (Biomist®), resmethrin (Scourge®) and sumithrin (Anvil®) made to control household and agricultural insects, and human lice (Bradberry, 2005). They are selectively toxic to insects due to higher nerve sensitivity to insects as compared to mammals. They are made from the flowers of pyrethrums (Chrysanthemum cinerariaefolium and C. coccineum).These include permethrin (Biomist®), resmethrin (Scourge®) and sumithrin (Anvil®) (Giampreti *et al*, 2013).

1.2.1.5. Sulphur compounds

This element is used to make pesticides in the form of wettable powder, paste or liquid against certain rust, leaf bright, fruit rots and powdery mildew. These include amidosulfuron,

diuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, ethoxysulfuron, flazasulfuron and cyclorsulfuron (Appleby *et al.,* 2002). These herbicides are non-selective and exterminate plants by slowing down the activities of ace*tolactate* synthase (ALS) enzyme. The other name for ALS is acetohydroxy acid synthase (AHAS). It is a protein found in plants and micro-organisms that invokes the initial step in the synthesis of amino acid having aliphatic side-chains with a branch such as isoleucine, valine and leucine.

1.2.2. Effects of Pesticides

The constant global use of pesticides raises eyebrows among the environmental scientists'. Almost over 90% of all sprayed pesticides (insecticide and herbicides) stray, hence reaching out to water, soil as well as non-targeted species (Miller, 2004). The transfer of pesticides from an area of application to any unintended site may contaminate other areas. Pesticide drift may cause water and soil pollution especially for persistent organic pollutants (POPs). According to Palmer *et al.,* 2007, the continued use of pesticide can reduce biological diversity; lead to pollinator decrease (Wells, 2007); destroy the natural environment (mainly for birds) (Palmer *et al.,* 2007) and cause a threat to endeared species (Miller, 2004). Naturally, pests become resilient and warrant a state-of-the-art brand of pesticide. Where another possibility of using a greater amount of the pesticide is sought to hinder the resistance, it may lead to environmental adulteration.

1.2.3. Transportation and Fate of Pesticides

Application of pesticides in the gardens, homes, turfs, offices, and hydrological sites become mobile in the ecosystem. *C*hlorinated hydrocarbon pesticides dissolve in fats and oils. Additionally, they persist in the environment leading to chronic toxicity (Aktar *et al.,* 2009). Amid marine animals, the concentration of pesticide are higher in carnivores including human beings, fishes, and more in birds that prey on fish and apex predators which include

carnivores and omnivores (Jawale *et al.,* 2017). Pesticides can also be transported from one region of the earth to another due to temperature difference, especially in the Polar Regions and mountain tops (Rodrigo *et al.,* 2012).

Volatile Pesticides get to higher temperature atmosphere and can be transported over relatively long range by wind to cold regions, where they precipitate and fall back to the earth by rain or as smog (Unsworth, 1999). In order to minimize harmful effects, it is expected that pesticides be degradable to facilitate quick deactivation in the environment. The objective of this research is to study the electrochemical behavior and decomposition of Tetrachlorovinphos in acetonitrile-water media using the electrocatalytic method.

1.3. Statement of the Problem

Pesticide residues have a long-term effect on the environment and thus pose a big challenge to ecosystem. The non- target residues may reach human tissues via food chain. The use of pesticides is detrimental and has long-term side effects to the unprotected organisms or environment (Kim *et al.,* 2017). A systematic review finding on "non-Hodgkin lymphoma and leukemia diseases studies" indicate a positive correlation with pesticide exposure" and thus warning on the excessive cosmetic use of pesticides (Bassil *et al*., 2007). According to WHO, FAO and UNEP (2004) report, there are approximately over 3 million agricultural workers in developing countries who experience severe pesticide poisoning every year (Miller, 2004). There also reports recorded from various food consumers who link their ailments with possibility of pesticide residue in both processed and non-processed food stuff (European Food Safety Authority (EFSA), 2013). The above condition has led to the rise of question on need for safety measures in order to build security and protection of consumers as the main target (Kalkbrenner, 2014). Although some studies have been done on the

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electrochemical behavior and rate of degradation of pesticides (Wangui *et al*., 2015), no detailed data is available on the same for Tetrachlorovinphos.

1.4. Main Objective

The overall objective was to study the electrochemical behavior and decomposition of Tetrachlorvinphos pesticide using electrocatalytic method.

1.4.1. Specific Objectives

The specific objective was to:

(i)   Determine the electrochemical properties of tetrachlorovinphos pesticide in acetonitrile-water media (1:1 v/v).

(ii)   Determine the voltammetric data for Cyanocobalamin.

(iii)   Determine the reduction potential of tetrachlorvinphos pesticide in absence and presence of cyanocobalamin catalyst.

(iv)   Determine the overall lowering potential during the reduction of tetrachlorvinphos pesticide in the presence of the Cyanocobalamin catalyst.

(v)   Determine the maximum wavelength of absorption for tetrachlorvinphos alone and with a Cyanocobalamin catalyst.

1.5. Justification and Significance

In developing countries like Kenya, contamination levels of organophosphate pesticides in food, soil, water and biota is making human beings vulnerable due to toxic effects of these chemicals (European Food Safety Authority (EFSA), 2013). The biotic and abiotic degradation pathways available are in adequate and this calls for additional alternative, electrochemical reduction method. Cyclic voltammetry method is simple to use, saves energy and produces much less poisonous products. To reduce toxicity, it is mostly preferable for

pesticides to be quickly inactivated in the environment and also prove the lowest limit of detection. The toxicity loss when quickly deactivated is dependent on both innate chemical properties and the prevailing environmental conditions (Sims & Cupples, 1999). The degradation process for some pesticides may take long time period (years), therefore demanding the use of catalysts to facilitate quick degradation and produce less harmful residual by-products in the environment.

Since the environment contributes much to our health, we are obliged to harmoniously work with consumer protection agencies in order to stay safe. There is also need for Kenya Bureau of standard (KEBS), Food and Agricultural Organization (FAO), and Pesticide Control Produce Board (PCPB) to partner with research institutions and production industries to ensure that only quality and environmental-friendly products reach the consumers. The introduction of catalysts will facilitate production of safe pesticide products that will be effective and less toxic to our ecosystem. For this reason, a study of decomposition of Tetrachlorovinphos pesticide in presence of Cyanocobalamin catalyst was made with an objective of determining the overall net change in reduction potential.

CHAPTER TWO

LITERATURE REVIEW

2.1. Uses of Pesticides in Kenya

Pesticide use is extensively found on large farms and parastatal organizations which are mainly concerned with export crops. The use of insecticides such as diuron, bylaton, vydate and hyvar is evident at Delmonte Pineapple farm in Thika (Ndungu, 2014), which has resulted in decline in aquatic life in local water sources.

One of the soil fumigants (Telone II or 1,3-Dicloropropene) used in the farm is restricted for use in Kenya by Pesticide Control Product Board (PCPB, 1998) due to its high level of toxicity and only allowed to be used by Delmonte Company alone (Ndungu, 2014). Pineapples harvested are either eaten raw or processed and taken to the world market for consumption and others consumed locally. This exposes consumers to its residue side effects. In some areas in western part of Kenya, Phenyl urea herbicides are commonly used to suppress weed growing in the sugarcane plantations. The Organochlorine pesticides used may find their way back to the water, soil and sediments via run-offs as reported along River Nyando at Muhoroni and Nyando at Ahero bridge (Getenga *et al*., 2004).

In central region of Kenya (Limuru), Dursban (Chlorpyrifos) finds a wide range use as an insecticide for the treatment of crops, lawns, ornamental plants and domestic animals. It assimilates strongly on the surface of loam soil particles and is sparingly soluble in water. It can most likely leach to soils and hence contaminating ground water (Mbui *et al.*, 2014). Naivasha town and its environs serve as a hub center for large scale horticultural farming. The industry uses large volumes of pesticides to produce quality vegetables, fruits and flowers that meet the international market standards especially in Europe. Despite the fact that the area has been witnessing good economic growth in terms of employment,

infrastructure and industrialization, the industrialization hub center has also posed a great health risk of pesticides to all who live in the center and within its environs. The resulting environmental pollution is a sum total of active ingredients in the pesticide, impurities and different components of product formulation at higher concentration than usual (Tsimbiri *et al.*, 2015).

2.2. Organophosphate Pesticides

Organophosphate or phosphate esters are also known as esters of phosphoric acid. They form basis of many insecticide, herbicides and warfare nerve agents in military practice (Balali-Mood and Balali-Mood, 2008). They also find wide applications in natural and synthetic industries because of the ease with which these organic groups can be linked together. This broad application exposes many users to long term ill health effects innocently.

The general structure of organophosphate as defined by Schrader's formula is as shown below:

$$R^1 \diagdown \underset{R^2 \diagup}{\overset{O \diagup (S)}{P}} \diagdown OX$$
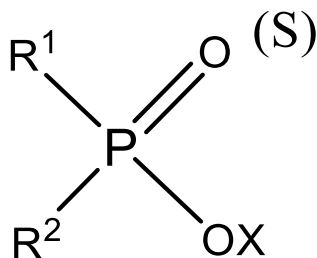
Figure 2.1: General structure of organophosphate compound

In the Figure 2.1., R^1 and R^2 represents CH_3- or CH_3CH_2 - groups, the O in the OX can be substituted for S in some compounds, whereas the H group can take other forms (Zacharia, 2011). Organophosphates are known for their acute toxicity to bees, wildlife and human beings (Kohler & Triebskorn, 2013). The adverse toxicity in invertebrates' and invertebrates' is by cholinesterase inhibition that leads to irreversible blockage of acetylcholinesterase across a synapse. Consequently, there is failure of movement of nervous impulses across the

synapse resulting to twitching of voluntary muscles and finally death especially in cases of high doses (Bird *et al., 2003*).

2.2.1. Organophosphates mode of action

A general structure of an organophosphates (Figure 2.1) is made up of a central phosphorous atom (P) and the P=O or P=S bond. The leaving group substituted nucleophilically by the Oxygen atom of serine in acetocholinesterase (AcHE) active site is represented by letter symbol H. A leaving group 'O' determines the rate at which inhibition occurs; slower leaving groups result in slower enzyme inhibition affinity and vice versa (Hreljac & Filipic, 2009). The presence of fluorine atoms (F) in the leaving group increases the organophosphate ability to hydrolyze and inhibit AcHE which leads to the death of an organism (Bird *et al., 2003*). When the organophosphates leaving group contains alkyl or aryl groups, it is perceived to be less toxic. The alkoxy groups are represented by side groups (R^1 and R^2). The most active configuration of organophosphate that binds to the active site of AcHE is the oxono structure. In the case where the organophosphate act as an AcHE inhibitor, the cytochrome P450 first metabolizes a potentially toxic thiono (P=S) (Figure 2.2) to corresponding oxon (P=O) (Figure 2.3) derivatives, thus becoming an inhibitor (Grupta, 2004).
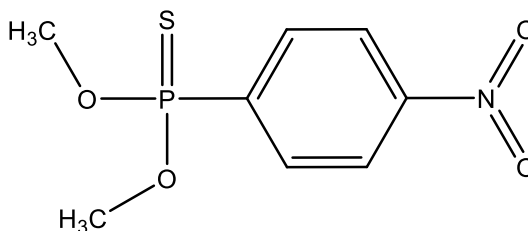
Figure 2.2: Methyl-parathion with a bonded S atom
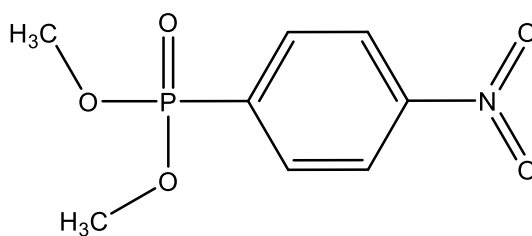
Figure 2.3: Methyl-paraxon with a bonded O atom

Cytochromes 450 (CYPs) are hemoproteins that use variety of micro- and macro-molecules such as substrates in enzymatic reactions (Rawling *et al*., 2011).

2.2.2. Tetrachlorvinphos Chemical Structure and Properties

Tetrachlorvinphos pesticide is an organophosphate insecticide whose systematic IUPAC name is (Z)-2-chloro-1-(2, 4, 5-trichlorophenyl) vinyl dimethyl phosphate. The structure of tetrachlorvinphos pesticide is as shown in Figure 2.4.
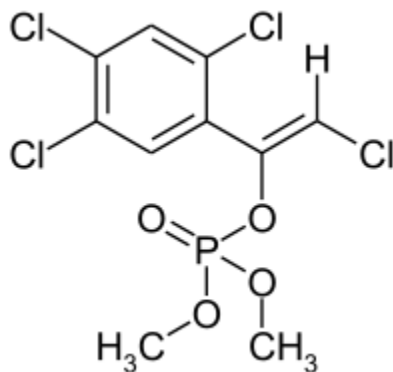
Figure 2.4: Chemical Structures of tetrachlorvinphos

Its chemical formula is $C_{10}H_9Cl_4O_4P$ and a molecular weight of 365.952 g/mol. It gradually hydrolyzes in neutral and aqueous acidic but rapidly in alkaline media (tetrachlorvinphos chemical Data Sheet, 2015).

2.2.3. Formulation and uses of Tetrachlorvinphos

According to Paranjape *et al.,* 2015, tetrachlorvinphos pesticide is registered and used in United States of America, Canada and South Africa. Formulations include wettable powder,

dusts, granules, impregnated materials in pet collars and emulsifiable concentrates (EPA, 2002). The pesticide finds a wide range application in agriculture, residential areas and in public health. In agriculture, it is used to control ecto-parasites in poultry and pet sleeping areas. It finds application in control of public health pests in and around dumpsites, recreational zones, and for common field treatments (Marrs, 2001).

2.2.4. Effects of Tetrachlorvinphos pesticide on living organisms

Symptoms of exposure to the living organisms include increased perspiration (diaphoresis), nausea, lachrymation (secretion of tears), salivation, blurred vision, diarrhea, pulmonary endema (accumulation of fluid in tissue air spaces of the lung), respiratory embarrassment and convulsions. It inhibits cholinesterase (AcHE) responsible for free relaxation of muscles after contraction and also promotes carcinogenesis in animals (Guyton *et al.,* 2015).

2.2.5. Degradation of Tetrachlorvinphos

This is a physical or chemical process by which a pesticide is transformed into an environmentally friendly substance that is reconcilable to the area of application (Burrows *et al*., 2002). The process involves both biotic (mediated by microorganisms) and abiotic (chemical and photochemical) transformation which are determined by structure and the prevailing environmental conditions (IUPAC, 2012). The reduction and oxidation gradients in sediments, aquifers and soils often determine which transformation occurs (Thomas *et al.,* 2010). The availability of sunlight in the topmost meter(s) of rivers or lakes, plant surfaces or sub-millimeter soil layers will mostly favors photochemical as well as photo-transformation (IUPAC, 2012). In abiotic transformation, the electronic absorption spectra of pesticide typically show little overlap with sunlight and are affected by direct photo-transformation (Burrows *et al*., 2002). Even though their desired effect is typically lowered, transformation products may remain problematic (Boxall *et al*., 2004). There is need for development and

incorporation of catalysts assist to aid in degradation of these persistent pesticides in the environment. The catalysis of vitamin B_{12} is effective in unsymmetrical cyclopropanation of unsaturated aliphatic hydrocarbon with Ethylene Diazo Acetate (Chen and Peter, 2004) and enzyme catalyzed reactions that rely on Co-C bond formation and cleavage of the Co-C bond (Giedyk *et al.*, 2015) and C-C and C-O bond formation (Scheffold *et al,* 1988). This is why remediation of the environmental pollutants by electrochemical reduction of Organic halogen compounds is attracting increasing attention of environmentalists and natural scientists' (Martin *et al*., 2016).

2.3. The Catalyst

Vitamin B_{12} is also called Cyanocobalamin. Vitamin B_{12} contains the biochemically rare element cobalt (Co); sitting in the center of corrin ring. It can be obtained as an amorphous red powder or dark red crystals. Its molecular formula is $C_{63}H_{88}CoN_{14}O_{14}P$, and the molar mass is 1355.38 g/mol. The Chemical structure of Cyanocobalamin is highlighted in Figure 2.5.
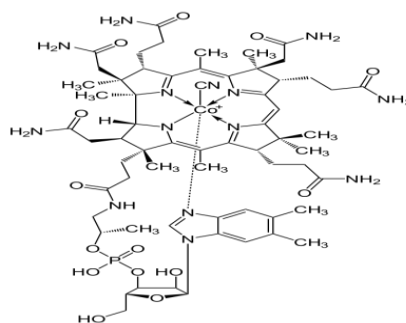
Figure 2.5: Chemical Structure of Cyanocobalamin

Cyanocobalamin undergoes reduction under favorable chemical conditions. The Co(III) is reduced to Co(II) or to Co(I). Co(II) and Co(I) are usually referred to as reduced and super-reduced forms respectively. Co(I) is known as $B_{12}s$ and Co(II) B_{12r} respectively.

The reduced and super reduced cyanocobalamins are both indefinitely stable in anoxic conditions. Reduced appears chromatic in solution, while Super reduced cyanocobalamin appears cyan under natural daylight, and violet under stimulated light (Figure 2.6).

Figure 2.6: Reduced forms of Cyanocobalamin, with a Co(I) (upper) center, Co(II) (middle) center, and Co(III) (lower) center. (McCormick and Wright, 1971).

This study involved the use of a catalyst and the homogenous media (acetonitrile/water) for the detoxification of tetrachlorovinphos. This new approach leads to less expensive, faster and safer ways of decomposing toxic pollutants. This is because electrocatalytic decomposition requires only a small amount of catalyst which is automatically recycled at the electrode. This suggests the newness of the current study as it provides a less expensive, faster and eco-friendly way for breaking down of toxic pollutants (Muya *et al.*, 2015).

A catalyst is meant to lower the reduction potential of an electrochemical process. In electrocatalysis, mediators transfer electrons between chemical substrates molecules and the electrodes (Valenti *et al.,* 2016). The catalytic transfer of electrons significantly lowers the potential needed to oxidize or reduce refractory substrates. Under controlled applied potential, the catalyst electrolysis current is magnified in the presence of substrate. In catalyst reduction process, the catalyst reduction occurs at the electrode and then shifts electrons to the substrate. The process restores the oxidized form of the catalyst, which is again reduced

at the electrode (Bruno, 2005). The reconversion of the catalyst between redox forms at potentials near its formal potential magnifies the current at the cathode (Hu & Rusling, 1991).

A specific form of a catalyst functioning at the electrode surfaces or may be electrode surface itself is called an electrocatalyst (Valenti *et al.,* 2016). Electrocatalysts can either be heterogeneous or homogenous. Heterogenous catalyst may include platinum surface, while homogenous catalyst includes co-ordination complex or enzyme (Bruno, 2005). Cyanocobalamin or Vitamin B_{12} was used as a catalyst in the electrocatalytic reduction of the Tetrachlorovinphos in the current research work. This is because; it is environmentally friendly, has higher catalyst stability and selectivity. The cyanocobalamin catalyst can also be recycled with water and retain moderate catalytic activity (Rusling, 1991).

The lavish electro-chemistries of vitamin B12 and their related compounds have been widely studied in various media. Their Interesting redox behavior is mostly found in their significant biochemical function and in their electrocatalytic applications (Lagunas *et al.,* 2006).

2.4. Analytical Techniques

It refers to the method used to determine the concentration of a chemical compound or chemical element (Braslavsky, 2006). These include titrimetric, chromatography, gravimetric, microscopy, radiometry (analysis of sample radionuclide content), spectroscopy (matter interaction with radiation) and electroanalytical analysis. As a chemical analyst, it's prudent to choose a technique based on the following factors; accuracy, precision, sensitivity, specificity and selectivity, robustness and ruggedness, scale operation, equipment, time and cost.

2.4.1. Spectroscopic Methods

This is the study of light and radiation interaction with matter (Hermann & Onkelinx, 1986). The technique employs electromagnetic radiations typically defined by electromagnetic regions. The members of the electromagnetic spectrum include radio waves, microwaves, infrared, infrared, visible light, ultraviolet, x-ray and gamma spectroscopy (Kenkel, 2003). Some of the spectroscopic methods used include mass spectroscopy (MS), nuclear magnetic resonance (NMR) and Ultraviolet/Visible spectroscopy (UV/Vis) (Skoog *et al.,* 2007).

2.4.1.1. Ultraviolet-Visible Spectroscopy

The technique involves light and radiation absorption or reflectance in the UV-Vis region. The chemical color perceived is basically determined by the quantity of radiation absorbed or reflected in the visible range of the electromagnetic spectrum. Atoms and molecules within electromagnetic spectrum undergo electronic transitions. In fluorescence spectroscopy, the electrons move from the excited state to ground state while in absorption spectroscopy, electrons move from ground state to the excited state (Skoog *et al.,* 2007).

2.4.1.1.1. Principle of Ultraviolet-Visible Spectroscopy

When light energy from a source passes through a molecule comprising of pi-electrons or non-bonding, the light energy is used to promote electrons to higher anti-bonding molecular orbitals (Fong *et al.,* 2011). The highest occupied molecular orbital (HOMO) is the pi-bonding while the lowest unoccupied molecular orbital (LUMO) is the (pie) π- antibonding. The pi- and sigma bonding orbitals contain the normal bonding pair of electrons, n-antibonding contain lone pair of electrons while pi- and sigma-antibonding are normally empty (Skoog, 2007). The ordered transitions from high to low energy are as follows: σ-σ^* > n-σ^* > π-π^* > n-π^* (Skoog *et al.,* 2007).

2.4.1.1.2. Instrumentation
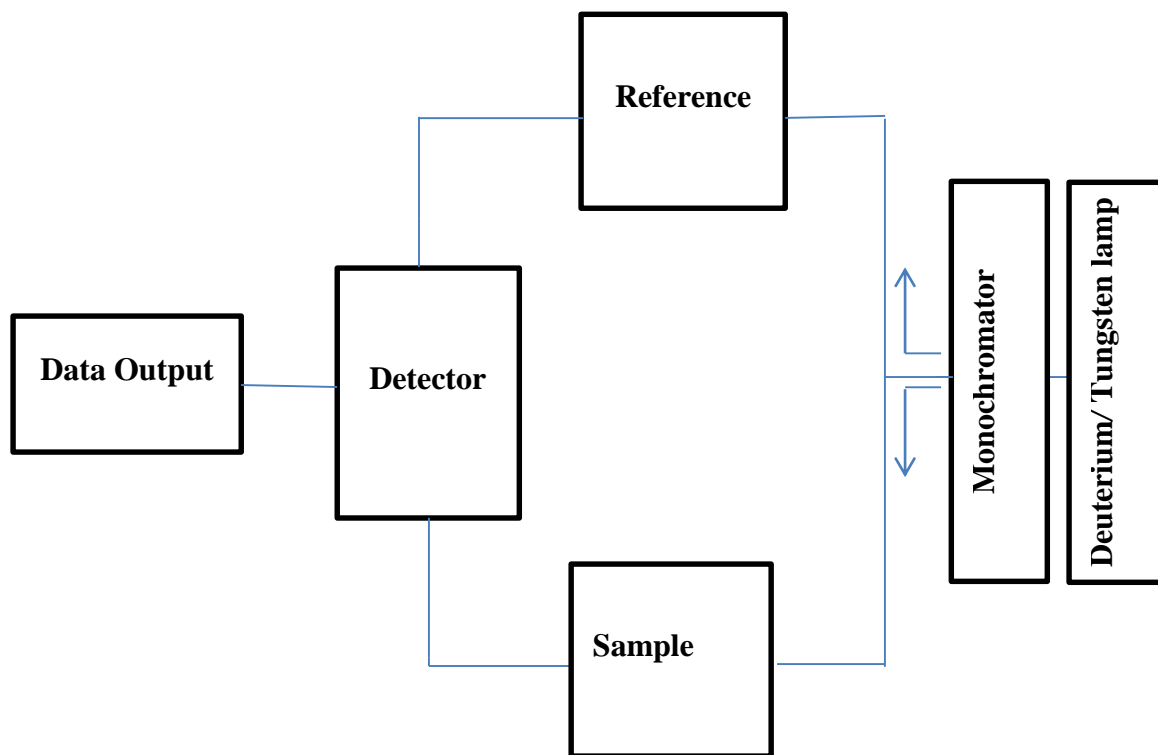
Figure 2.7: The double-beam UV-Visible spectrophotometer

The double-beam spectrophotometer uses two beams of light. These are reference and sampling beam that traverses the sample (Skoog *et al,* 2007). The intensity of the reference beam is taken as zero absorbance or 100% transmission. The recorded value is the ratio of the two beam intensities. In some double-beam spectrophotometers with two detectors, the measurement of two beams is done simultaneously. In alternative instruments, both reference and sampling beams traverse the optical chopper, which obstructs the beam one at a time. The detector repeatedly measures the sample beam and the reference beam in conformity with the beam splitter. When one or more dark fringes occurs in the cycle of a beam splitter, then, the measured beam intensities ought to be corrected by subtracting the intensity measured in the dark interval before the ratio is taken. The samples in liquid form are the

most preferred form of samples in Ultraviolet and Visible spectrophotometry. Samples are held in a cuvette commonly with internal width of 1cm. The most preferred cuvettes are made of good quality Quartz due to their transparency throughout ultraviolet, visible and near infrared regions of the electromagnetic spectrum. Plastic and glass cuvettes are limited to the use in extremely dilute samples where extreme sensitivity is paramount. They are also found to absorb in UV, which makes them inefficient within visible wavelengths.

2.4.2. Electroanalytical Methods

Zoski, (2007) defines electroanalytical method as a branch of analytical chemistry that involves measurement of potential and/or corresponding current in an electrochemical cell containing the analyte. Potentiometry, coulometry, and voltammetry are among categories of the common electroanalytical methods available.

2.4.2.1. Potentiometry

Potentiometry involves potential measurement between two electrodes while controlling the electric current between them (Noyhouzer, 2013). A reference electrode has a stable potential, while the potential of the indicator electrode varies with the sample composition. Consequently, potentiometry uses indicator electrodes that are selective to a specific ion, in order for the potential to rely only on the specific ion activity. The electrode equilibration time with the solution mostly affect the accuracy or sensitivity of the measurement. That is why in marine environment, platinum electrode is frequently used because of its high electron transfer kinetics (Grundl, 1994).

2.4.2.2. Coulometry

Coulometry measures the quantity of electric charges consumed or produced during an electrolysis process. The conversion of analytes from one oxidation state to another is enhanced by applied potential. The amount of current flow is recorded directly or indirectly in order to ascertain the number of electrons passed. The sample concentration is then correlated to the number of electrons passed. Most common form of coulometry is the bulk electrolysis or potentiostatic coulometry (Jagner *et al.,* 1996).

2.4.2.3. Voltammetry

Voltammetry measures the resulting current by applying a constant and/or changing potential at the electrode surface. The resulting values can easily be used to determine the electrochemical reactivity and reduction potential of the analyte (Da Silva *et al.,* 2008). The method is non-destructive, sensitive, economical and chemical species-selective. The experiment can be carried out even with small analyte volumes (1 -10 ml) of low concentrations (0.0001 – 0.001 M/L). Any material that has the ability to conduct electricity and does not react or dissolve in the analyte solution can analyze both organic and inorganic samples (Noyhouzer, 2013). The disadvantage of this method is that, the solution containing the analyte is usually discarded since it is not easy to separate from the bulk electrolyte.

2.4.2.3.1. Cyclic Voltammetry

Cyclic voltammetry is a robust and well favored electro-chemical technique in the study of redox processes of chemical species (Da Silva *et al.,* 2008). It compares favorably with the spectra of optical spectroscopy. In cyclic voltammetry, the working electrode potential is cycled, and the resulting current is registered over a given time period. The resulting plot of the corresponding current and applied potential values gives rise to a voltammogram similar to that of Figure 2.8 below. The forward scan runs within a range of 0.8 to - 0.2 Volts, while

the reverse scan occurs within a range of - 0.2 to 0. 8 Volts. A complete cycle scan is made up of a single forward and reverse scan. In Figure 2.8, (a) is the lower potential while (d) is the switching potential. The potential sweeps negatively between (a) and (d) via (b) and (c) causing a reduction process. The potential sweeps positively between (d) to (g) via e and (f) causing an oxidation process.
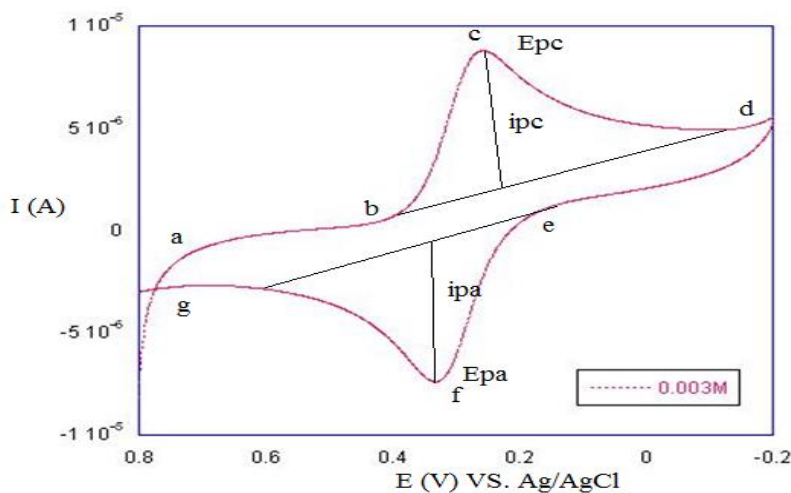
Figure 2.8: Cyclic Voltammogram for the reduction of Ferricyanide in potassium nitrate solution using Carbon electrode.

In Figure 2.7 above, in the reduction process the peak cathodic current (i_{pc}) corresponds to peak cathodic potential (E_{pc}), while during the oxidation process the peak anodic current (i_{pa}) corresponds to peak anodic potential (E_{pa}). The peak point (c) is attained when the analytes at the electrode surface are reduced fully, while peak point (f) is reached when all analyte at the electrode surface has been oxidized.

CHAPTER THREE

METHODOLOGY

3.1. Cyclic Voltammetry Chemicals and Reagents

Potassium ferric cyanide, analytical grade was purchased from BDH Company, Potassium Nitrate, and acetonitrile from Fisher Scientific Company. Water was deionized by Elga water purification apparatus. Tetrachlorvinphos pesticide standard and cyanocobalamin was obtained from Sigma Aldrich. All acquired reagents were used without further purification. Analytical balance of high degree of precision ($\pm$ 0.0001 g) was used to measure weight of samples. The replicates were made 3 times in each experiment.

3.1.1. Solution Preparation for Cyclic Voltammetry

In this experiment, the analytical grade of acetonitrile (CH_3CN) with dielectric constant of 36.6 at (25 ℃), dipole moment of 3.92 debyes (D) and a low viscosity of 0.37 centipoise (Cp) at (25℃) (Hu *et al.,* 2016) was selected as a suitable solvent. Its high dielectric constant and low viscosity makes it readily miscible with deionized water hence forming a good electrolyte solvent which is inert under the oxidation and a reduction condition used in this experiment. One liter acetonitrile- water (1:1 v/v) solution was made by adding 500 ml of deionized water to 500 ml of acetonitrile solvent into a 1 liter volumetric flask. The miscible solvent (acetonitrile-water) was used to make all other solutions. To prepare a liter of 0.1 M potassium nitrate supporting electrolyte; exactly weighed 10.212 grams of potassium nitrate (99.5% purity), transferred it to a clean 1 liter volumetric flask and added small volumes of acetonitrile-water media while constantly stirring until all the solute dissolved completely and then topped up to one liter volume. Part of this "cock tail" (acetonitrile-water 1:1 v/v in 0.1 M potassium nitrate) was used to prepare a 100 ml stock solution of 0.01 M potassium ferric cyanide, 0.01 M tetrachlorvinphos alone, and 0.001 M cyanocobalamin. To make a 100 ml stock solution of 0.01 M potassium ferriccyanide; exactly weighed 0.3326 grams of ferric

cyanide (bright red) crystals and dissolved it in small volume of "cocktail" (acetonitrile-water 1:1 v/v in 0.1 M potassium nitrate) at room temperature in a 100 ml volumetric flask and then topped up to the mark. The color of the resulting solution turned to green-yellow. A volume of 1, 2, 3, 4 and 5 ml stock solution of 0.001 M potassium ferricyanide was put into separate 100 ml volumetric flasks and topped up to the mark using the "cocktail" in volumetric flasks to make concentrations of 0.001, 0.002, 0.003, 0.004 and 0.005 M potassium ferric cyanide respectively by serial dilution. Potassium ferric cyanide solution was used as a standard to verify the performance of the potentiostat instrument.

To prepare a 100 ml stock solution of 0.01 M tetrachlorvinphos alone; weighed exactly 0.3674 grams of tetrachlorvinphos chemical standard (99.6% purity) in a 100 ml volumetric flask and then dissolved it in the "cocktail". The solution was colorless. A volume of 1, 2, 3, 4 and 5 ml was put into a 100 ml volumetric flask and topped up using acetonitrile-water media in 0.1 M potassium nitrate to make a 0.001, 0.002, 0.003, 0.004 and 0.005 M tetrachlorvinphos respectively by serial dilution. To make a 100 ml stock solution of 0.001 M cyanocobalamin; weighed exactly 0.1361 grams of cyanocobalamin crystals (99.5 % purity) in a 100 ml volumetric flask, dissolved it in "cock tail" (water-acetonitrile (1:1 v/v) in 0.1 M potassium nitrate). The stock solution cyanocobalamin was used to make a 0.0001 M cyanocobalamin by adding 1 ml of cyanocobalamin to a 100 ml volumetric flask and topping up to the mark with the "cock tail" (water-acetonitrile in 0.1 M potassium nitrate). To make 100 ml stock solution of 0.01 M tetrachlorvinphos with 0.001 M cyanocobalamin; weighed exactly 0.3674 grams of tetrachlorvinphos chemical standard (99.6% purity) in 100 ml volumetric flask and dissolved it in about 30 ml of acetonitrile-water (1:1 v/v) media in 0.1 M potassium nitrate and then added exactly 0.1361 grams of cyanocobalamin crystals (99.5 % purity) in the same volumetric flask and topped up to the mark. The mixture was swirled

to mix and form a homogenous solution (wine red). From the mixed solution matrix, aliquot volume of 1, 2, 3, 4 and 5 ml was put into separate 100 ml volumetric flask and topped up to the mark to make concentrations 0.001, 0.002, 0.003, 0.004 and 0.005 M tetrachlorvinphos with cyanocobalamin respectively. To make alumina slurry for cleaning the glassy electrode; weighed about 5 grams of 0.05µm aluminum oxide (98 % purity) in a 5 ml beaker and then added small amount of deionized water bit by bit while stirring until slurry formed. The slurry was poured on an electrode cleaning pad during the electrode cleaning process.

3.1.2. Instrumentation and Procedure

Cyclic voltammetry studies were done using a CHI 1232B Potentiostat model from CHI instruments, USA. The reference electrode was made up of silver/Silver Chloride, counter electrode made up of Platinum wire of diameter (Ø) 0.04 cm and working electrode made up of glassy carbon (GC) of diameter (Ø) 0.30 cm and surface area of (0.071 cm^2). The reaction cell used was designed to hold the electrodes and concurrently allow gently bubbling of pure nitrogen gas. The cell of capacity 10 ml or 100 µL was used for characterization because the analyte was available in small quantities. The electrodes were positioned in such a way that the tip of the reference electrode was very close to the working electrode. The reference, counter, working electrodes and the cell were thoroughly cleaned and rinsed with deionized water to provide a clean working environment. The working surface of glassy carbon electrode was polished using alumina slurry for about two minutes to have a new working surface (a mirror finish) before every scan. All the cyclic voltammetry studies were done at ambient temperature (24 ± 1^0C).

The operating procedure for cyclic voltammetry using CHI 1232B Potentiostat model from CHI instruments, USA were used in operating the instrument. The instrument was started-up by turning the switch on and allowing the instrument to initialize before opening the

software. The potential window and current settings were selected for each experiment and a run was initiated by clicking a "start" button while "stop" button was used to stop a run. A Solution of 0.1 M Potassium nitrate (KNO_3), supporting electrolyte in acetonitrile-water (1:1) was run first to establish the potential working window.

In scan-rate studies, the reaction cell was filled with a 5 ml of 0.001 M potassium ferriccyanide in 0.1 M potassium nitrate and gently bubbled a stream of pure nitrogen gas for about 10 minutes to remove oxygen before taking measurements which would give a broad cathodic peak at around − 0.50 V versus Ag/AgCl. A single cyclic voltammetry scan at 0.01 V/s for the 0.001 M potassium ferriccyanide in 0.1 M KNO_3 was acquired by clicking the "run" button between potential of - 0.2 and 0.8 V. On the same scale and settings, cyclic voltammograms were obtained for the same solution at 0.02, 0.03, 0.04 and 0.05 V/s successively. The cell emptied and cleaned, the electrodes were also cleaned between different concentrations. The experiment was repeated for each concentration (0.002, 0.003, 0.004 and 0.005 M) to achieve the best voltammograms for overlay.

For concentration studies, a clean cell and electrodes were used to acquire cyclic voltammograms at 0.01V/s of 0.001 M of potassium ferriccyanide in 0.1 M KNO_3 on separate recording page. The cyclic voltammograms were obtained on the same axis and settings, for 0.002, 0.003, 0.004 and 0.005 M potassium ferricyanide solutions. The experiment was repeated for each concentration at varying scan rates of 0.02 to 0.05 V/s to achieve the best voltammograms for overlay.

The direct reduction and electrocatalytic reduction of tetrachlorvinphos pesticide was carried out between the potentials of - 0.40 to - 1.50 Volts. For scan-rate studies, a single cyclic voltammogram at 0.01 V/s was acquired for the 0.001 M tetrachlorvinphos pesticide alone in 0.1 M potassium nitrate. On the same scale and settings, cyclic voltammograms for the same solution were obtained at 0.02, 0.03, 0.04 and 0.05 V/s sequentially. The experiment was repeated for each concentration (0.002, 0.003, 0.004 and 0.005 M) to achieve the best voltammograms for overlay. The procedure for tetrachlorvinphos was also used to study tetrachlorvinphos pesticide with cyanocobalamin.

For concentration studies of 0.001 M tetrachlorvinphos, the cell was emptied and cleaned, and also ensured that the all the electrodes (Ag/AgCl, platinum and glassy carbon were also rinsed clean. A cyclic voltammetry at 0.01 V/s of 0.01 M of tetrachlorvinphos solution was recorded on different page. Cyclic voltammograms of tetrachlorvinphos pesticide for the 0.002, 0.003, 0.004 and 0.005 M of tetrachlorvinphos pesticide sequentially were made on the same axis. The experiment was repeated for each concentration at varying scan rates (0.02 to 0.05 V/s) to achieve the best voltammograms for overlay. The above procedure was also used for tetrachlorvinphos pesticide with cyanocobalamin. The reduction of 0.0001 M cyanocobalamin was carried out between the potentials of - 0.40 to - 1.60 Volts using the above procedure for Tetrachlorvinphos pesticide alone and with a catalyst.

The data obtained was recorded, analyzed and interpreted using kaleidagraph software, version 4.1.1 and Microsoft Excel 2010 statistics software. The data obtained for potassium ferriccyanide was used to calculate the formal redox potential ($E^{0'}$) and compared with the

standard electrode potential (E) of the redox couple. The peak separation (ΔE_p) was also calculated. From the overlay cyclic voltammograms for different scan rates of 0.001 M ferriccynide solution, the peak anodic (ipa) and cathodic (i_{pc}) current for all scan rates was measured. The plots of i_{pc} versus the square root ($V^{1/2}$) and (i_{pa}) versus the square root ($V^{1/2}$) were made. From the slope of the plot of of i_{pc} versus the square root ($V^{1/2}$) and Randle-Sevcik equation; $i_{pa} = (2.69 \times 105) \, n^{3/2} A D^{1/2} C V^{1/2}$) the diffusion coefficient (D) for the redox was calculated in their right units. The procedure above was also used to characterize the voltammograms for cyanocobalamin tetrachlorvinphos alone and with a catalyst respectively.

3.2. UV-VIS Spectrophotometric Method

3.2.1. Solutions

A liter acetonitrile- water (1:1 v/v) solution was made by dissolving a volume of 500 ml of deionized water into 500 ml of acetonitrile solvent into a 1 liter volumetric flask. The miscible solvent (acetonitrile- water) was used to make all other solutions. To prepare half a liter of 0.1 M potassium nitrate; exactly weighed 10.2120 grams of potassium nitrate (99.5% purity), transferred it to a clean 1 liter volumetric flask and added small volume of acetonitrile-water media while constantly stirring until all the solute dissolved completely and then topped up to one liter volume using acetonitrile-water (1:1). A combination of solutions is known as "cocktail". This "cock tail" (acetonitrile-water 1:1 v/v in 0.1 M potassium nitrate) is the solvent that was used to prepare a 100 ml stock solution 0.01 M tetrachlorvinphos alone, 0.01 M tetrachlorvinphos with cyanocobalamin and 0.001 M cyanocobalamin. To prepare a 100 ml stock solution of 0.01 M tetrachlorvinphos alone; weighed exactly 0.3674 grams of tetrachlorvinphos chemical standard (99.6% purity) in a 100ml volumetric flask and then dissolved it in the "cocktail". The solution was colorless. Each volume of 1, 2, 3, 4 and 5 ml was put into separate a 100 ml volumetric flask and

topped up using acetonitrile-water media in 0.1 M potassium nitrate to make a 0.001, 0.002, 0.003, 0.004 and 0.005 M tetrachlorvinphos respectively by serial dilution. To make a 100 ml stock solution of 0.001 M cyanocobalamin; weighed exactly 0.1361 grams of cyanocobalamin crystals (99.5 % purity) in a 100ml volumetric flask, dissolved it in water-acetonitrile (1:1 v/v) in 0.1 M potassium nitrate. This stock solution was used to make a 0.0001 M cyanocobalamin by diluting 1 ml of 0.0001 M cyanocobalamin in 100 ml of water-acetonitrile in 0.1 M potassium nitrate. To make 100 ml stock solution of tetrachlorvinphos with cyanocobalamin; weighed exactly 0.3674 grams of tetrachlorvinphos chemical standard (99.6% purity) in 100 ml volumetric flask and dissolved it in about 30 ml of acetonitrile-water (1:1) media in 0.1 M potassium nitrate and then added exactly 0.1361 grams of cyanocobalamin crystals (99.5 % purity) in the same volumetric flask and topped up to the mark. The mixture was swirled to mix and form a homogenous solution. From this solution matrix, each volume of 1, 2, 3, 4 and 5 ml was put into a separate 100 ml volumetric flask and topped up to the mark to make concentrations of 0.001, 0.002, 0.003, 0.004 and 0.005 M tetrachlorvinphos with cyanocobalamin respectively.

3.2.2. Instrumentation and Procedure for UV-Vis Spectrophotometer

The UV-Vis analysis was done using UV-1700 spectrophotometer; double beam model at the Analytical Chemistry laboratory, University of Nairobi. Two quartz cuvettes were used in this experiment; one cuvette was filled with about 5.0 ml of sample solution while the other was filled with about 5.0 ml blank. The replicates were made 3 times in each experiment.

For the spectrum of 0.0001 M cyanocobalamin and 0.005 M tetrachlorvinphos pesticide alone, the blank consisted of homogenous solution of acetonitrile-water (1:1 v/v) in 0.1 M KNO$_3$ while the sample was tetrachlorvinphos pesticide alone. For the 0.005 M tetrachlorvinphos pesticide with cyanocobalamin; the blank consisted of homogenous

solution of 0.005 M tetrachlorvinphos pesticide and acetonitrile-water (1:1 v/v) in 0.1 M KNO$_3$ while the sample was tetrachlorvinphos with pesticide. The sample cell was placed in sample holder while the respective blank cell in the reference cell holder. The scan was done for each set of sample using the highest concentration to generate a respective absorbance spectrum. The absorbance spectrum of 0.005 M of tetrachlorvinphos without a catalyst was done for every 10 nm throughout the UV- range of 200 – 400 nm in order to increase the number of data points.

The absorbance spectrum for 0.0001 M cyanocobalamin alone and tetrachlorvinphos with a cyanocobalamin was done for every 20 nm throughout a UV- range of 300 to 700 nm. The scanned absorption spectrum were studied and a conclusion drawn from the findings. The greatest absorption wavelength for each spectrum was identified, and used to run absorbance versus concentration studies of tetrachlorvinphos pesticide alone and tetrachlorvinphos with cyanocobalamin. The spectrums were drawn on separate pages.

CHAPTER FOUR

RESULTS AND DISCUSSION

The chapter discusses the results of cyclic voltamograms of potassium ferricyanide for validation, as a standard followed by those of tetrachlorvinphos pesticide in presence and absence of cyanocobalamin. The results of UV- Spectrum of the pesticide alone and pesticide in presence of cyanocobalamin is also discussed. The replicate for cyclic voltammetry and UV-Vis studies was made 3 times in each experiment.

4.1. Cyclic Voltammetry

4.1.1. Ferricyanide

Potassium ferricyanide is used as a standard in electrochemistry because of its fast electron transfer kinetics (Grundl, 1994). It involves the study of one-electron reversible redox system. This preliminary work was done to introduce the fundamental principles of cyclic voltammetry and also validate the instrument (Figure.4.1.).
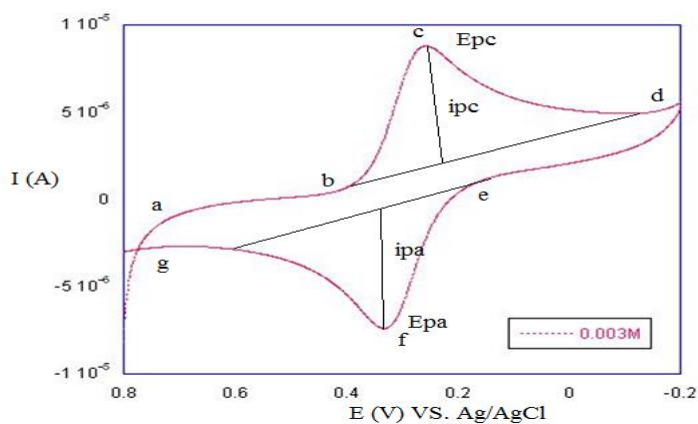
Figure 4.1: Cyclic voltammogram for the reduction of ferricyanide in potassium nitrate solution on glassy carbon electrode at a Scan rate of 0.01 V/s

The symmetry in Figure 4.1 represents an electrode process that is diffusion-controlled at the planar electrode surface. The most important variables in *a* reversible cyclic voltammetry

wave is the cathodic peak potential (E_{pc}), anodic peak potential (E_{pa}), cathodic peak current (i_{pc}) and the anodic peak current (i_{pa}). In a redox couple process, the peak current (i_p) is evaluated using the Randles-Sevcik equation below:

$$i_p = (2.69 \times 10^5) \, (n^{3/2} A D^{1/2} C V^{1/2}).$$

In this equation, Constant $= 2.69 \times 10^5$; n is the number of moles of electrons transferred per mole of electroactive species; A is the area of the electrode in cm^2; D is the diffusion coefficient in cm^2/s; C is the solution concentration in mole/L; and V is the scan rate of potential in Volts/second. This concept of redox system reversibility may also be determined by calculating the ratio of cathodic and anodic peak currents. In ideal redox process, the anodic and cathodic peak current ratio is unity: i.e. $/i_{pa}/i_{pc}/ = 1$ (Nkunu *et al*, 2017).

4.1.1.1. Effects of concentration of potassium ferricyanide solution at a scan rate of 0.001 V/s on peak currents.

The cyclic voltammogram overlay of potassium ferriccyanide in Figure 4.2 clearly shows that the peak current increases with increase in concentration (0.001 – 0.005 M) and vice versa.

Figure 4.2: Effects of Concentration of potassium ferricyanide solution at a scan rate of 0.001 V/s on peak currents.

It is highly noted from Figure 4.2., that, the peak current height increases with increases in concentration (0.001 – 0.005 M).

Table 4.1: Concentration studies of 0.001 M potassium ferriccyanide at a scan rate of 0.01 V/s.

Concentration (Mol/l)	Epa (V)	Epc (V)	ipa (A)	ipc (A)	/ipa/ipc/	$E^{\circ'}$ (V)	ΔEp (V)
0.001	0.330	0.259	-4.750E-6	4.880E-6	0.973	0.295	0.071
0.002	0.329	0.259	-6.490E-6	6.725E-6	0.965	0.294	0.070
0.003	0.332	0.259	-7.761E-6	8.094E-6	0.959	0.296	0.073
0.004	0.334	0.256	-9.702E-6	1.007E-5	0.968	0.295	0.078
0.005	0.333	0.258	-1.005E-5	1.026E-5	0.980	0.296	0.075

Key:

E_{pa} = anodic peak i_{pa} = peak anodic current

E_{pc} = cathodic peak i_{pc} = peak cathodic current

ΔE_p = peak separation $E^{0'}$ = Formal redox potential

/i_{pa}/i_{pc}/ = ratio of anodic peak current and cathodic current

For concentration studies (Table 4.1), the /ipa/ipc/ ratios values range from 0.959 to 0.980 which when rounded-up to 1 decimal place results to unity for reversible redox process. It was also observed that the absolute values for i_{pc} were greater than the corresponding i_{pa}.
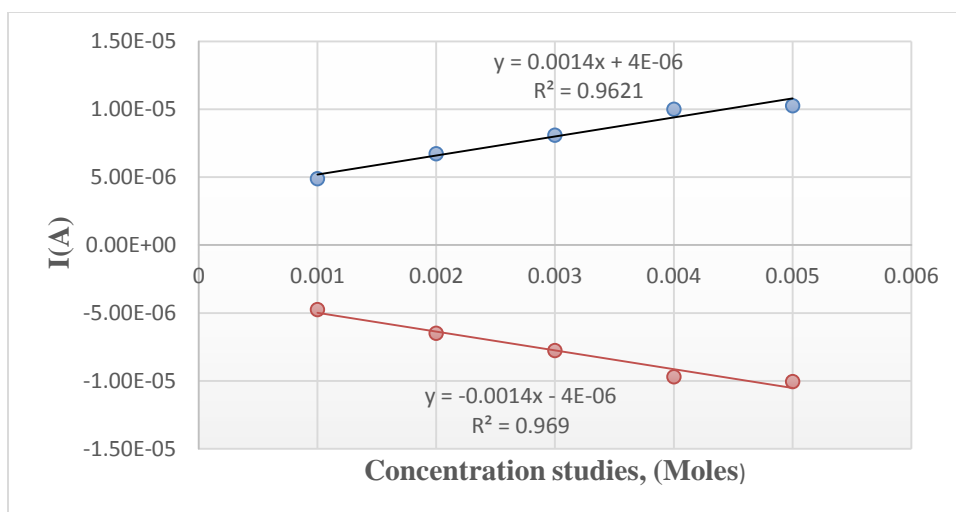
Figure 4.3: The anodic (red) and cathodic (blue) currents against concentration

The Peak current (i_p) is linearly proportional to the $V^{\frac{1}{2}}$ for a diffusion controlled process in both concentration and scan rate studies (Figure 4.3). There is a good correlation coefficient between peak (i_{pa} and i_{pc}) and concentration. This denoted by R^2 value of 0.9621 and 0.965 respectively. However, correlation does not show causation (Bland & Altman, 1996).

4.1.1.2. Effects of scan rate on the potassium ferricyanide peak currents

The cyclic voltammogram of 0.001 M potassium ferriccyanide in Figure 4.4 clearly shows that the peak current increases with increase in scan rate (0.01 – 0.05 V/s) and vice versa.
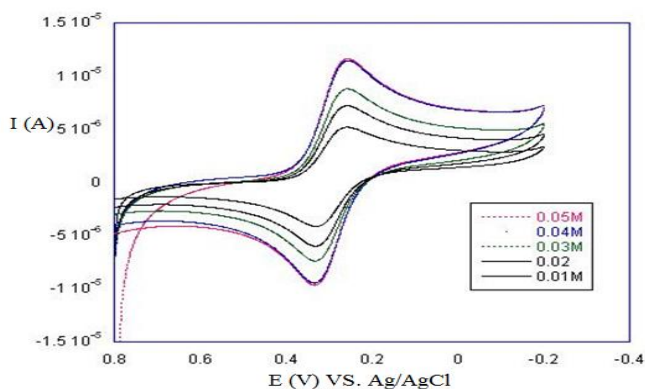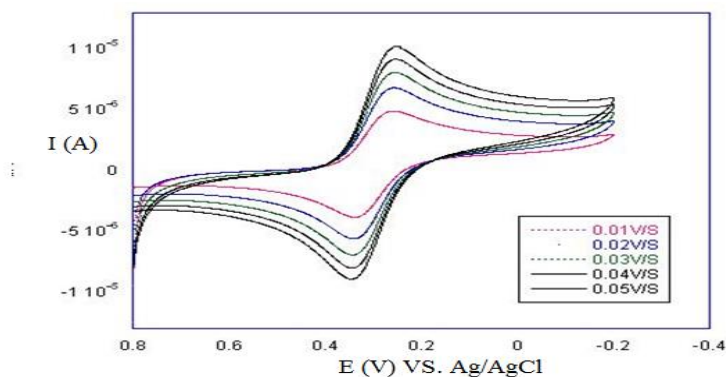

Figure 4.4: Effect of scan rate on peak currents for ferricyanide solution at a scan rate of 0.001V/s.

Table 4.2: Variation of scan rate for 0.001 M K₃Fe (CN)₆ in 0.1 M KNO₃ Versus Ag/AgCl.

Scan rate (V/S)	Square-root of scan rate ($V^{1/2}$)	Epa (V)	Epc (V)	ipa (A)	ipc (A)	/ipa/ipc/	E°' (V)	ΔEp (V)
0.01	0.100	0.339	0.259	-4.434E-6	4.566E-6	0.9711	0.299	0.080
0.02	0.141	0.341	0.256	-5.952E-6	6.387E-6	0.931	0.299	0.085
0.03	0.173	0.342	0.255	-7.064E-6	7.645E-6	0.924	0.299	0.087
0.04	0.200	0.346	0.253	-7.961E-6	8.659E-6	0.919	0.300	0.093
0.05	0.224	0.346	0.253	-8.750E-6	9.557E-6	0.916	0.300	0.093

Key:

E_{pa} = anodic peak i_{pa} = peak anodic current
E_{pc} = cathodic peak i_{pc} = peak cathodic current
/i_{pa}/i_{pc}/ = ratio of anodic peak current and cathodic current
$E^{0'}$ = Formal redox potential
ΔE_p = peak separation

For the scan rate studies (Table 4.2), it is evident that the peak (i_{pa}) values ranges from 4.434 x 10^{-6} to 8.750 x 10^{-6}A and 4.566 x 10^{-6} to 9.557 x 10^{-6} A for i_{pc}. The /i_{pa}/i_{pc}/ ratios range from 0.916 and 0.97; which when rounded up to the nearest whole number would result to unity or 1.

A plot of peak current (i_{pa} and i_{pc}) is linearly proportional to the corresponding square root of the scan rate (Figure 4.5). The plots in Figure 4.5 have corresponding R^2 value that is above 0.95 and close to unity (1). This implies good correlation coefficient for a diffusion controlled process.
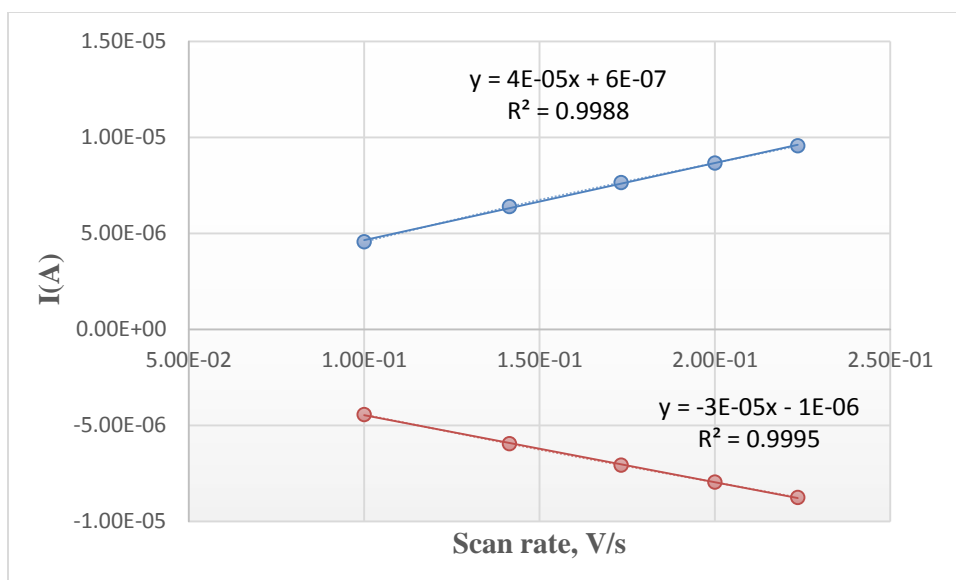
Figure 4.5: Anodic (red) and cathodic (blue) currents against square root of the scan rate.

The Experimental value for anodic and cathodic current density in concentration studies (Figure 4.2) is 1.13 ± 0.05 and 1.10 ± 0.08 A/m^2 respectively. While the diffusion coefficient for ferricyanide and ferrrocyanide is 6.53×10^{-6} and 5.35×10^{-6} cm s^{-1} respectively in 0.1 M KNO$_3$ versus Ag/AgCl. The diffusion coefficient values obtained from experiment compares slightly closer to 7.55×10^{-6} cm^2 s^{-1} and 6.81×10^{-6} cm^2 s^{-1} respectively in 0.1M KNO$_3$ versus SCE as reported by Wanjau *et al.,* 2015. The difference in the values may be attributed to change in viscosity and conductivity during the process of electrolyte decomposition.

A formal potential is the reduction potential that applies under a defined set of conditions that includes: pH, ionic strength, and concentration of the complexion. For a reversible process, formal potential ($E^{0'}$) is given by averaging anodic and cathodic peak potentials. The experimental value computed is 0.300 ± 0.00 V and 0.29 ± 0.00 V in 0.1 M KNO$_3$ versus Ag/AgCl for scan rate studies and concentration studies respectively. Rock (1966) obtained -

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0.3704 ± 0.05 V at 25 °C and Wei *et al.,* 2018 obtained 0.25 V for 0.2 M K$_4$Fe (CN)$_6$ in 3 M KOH aqueous solution. These values compare favorably to 0.332 ± 0.007V reported by Wanjau *et al.*, 2015 in 0.1 M KNO$_3$ versus SCE. The formal potentials of ferro-ferric cyanide also depend on the concentration of the acid as well as the nature of the anions (Wei *et al,* 2018).

The other property of a reversible process is, the peak potential separation ($\Delta E_p = (E_{pa} - E_{pc})$ between peak currents. The ideal value for a reversible process (one-electron) is around 0.059 V (Thakurathi *et al.,* 2018). Wanjau *et al.,* (2015) reported 0.070 ± 0.005 V for concentration studies. The value from this study is 0.073 ± 0.003 V and 0.088 ± 0.006V for scan rate and concentration studies respectively. The value (s) slightly differs from theoretical value because of non-linear diffusion, uncompensated solution resistance and normal variation in polishing of the electrode (Cumba *et al.,* 2016). In consideration of the above preliminary work was strongly concluded that the procedure favors the current study.

4.1.2. Cyanocobalamin

The reduction of a 1.0 x 10^{-4} M of Vitamin B$_{12}$ on the glassy carbon electrode surface in acetonitrile-water (v/v 1:1) containing 0.1 M KNO$_3$ at a potential ranging from 0 to -1.60 V versus Ag/AgCl exhibited a voltammogram symmetry in (Figure 4.6).

Figure 4.6: Cyclic voltammogram for 0.0001 M cyanocobalamin in acetonitrile-water solution containing 0.1M KNO₃ at scan rate of 0.03V/s versus Ag/AgCl.

In Figure 4.6, there were two values observed for E_{pc} at around - 0.526 V and - 0.892 V and an E_{pa} about - 0.600 V. The corresponding anodic peak (E_{pa}) is smaller compared to its corresponding cathodic peak. The peak potential difference shows that it is dependent on concentration (quasi reversible). The reduction of Vitamin B_{12} results on the change in the oxidation number of central cobalt species from 3^+ to 2^+ and then from 2^+ to 1^+ (Muya *et al.*, 2015). Presence of strong ligands such as CN^- induces large shift of Co^{III}/Co^{II} in Vitamin B_{12} leading to integration of Co^{III}/Co^{II} and Co^{II}/Co^{I} to an instant two-electron reduction (Lexa, 1980). The symmetry of the voltammogram obtained in (Figure 4.7) is similar to that reported by Lagunas *et al.*, 2006. These non-symmetric reduction and oxidation peaks for cyanocobalamin is a true indication of a quasi-reversible process due to non-linear diffusion

and uncompensated solution resistance (Kissinger & Heineman, 1983). It is also observed that $i_{pa}/i_{pc} \neq 1$ (Muya *et al.,* 2015).

The quasi-reversible process can be explained on the basis of characteristics of transition metals which are known to shift the geometry of their co-ordination sphere, with electron moving from one atom or molecule to another followed by gain or loss of axial ligand (Davies *et al.,* 2002). The co-ordination sphere geometry of Co(III) is octahedral; Co(II) is square pyramidal and Co (I) a square planar (Davis *et a*l., 2002).

Another explanation can be based on the Oxidation and Reduction ('O' and 'R') of the electroactive species. In equilibrium position, the rate of conversion of 'O' to 'R' species is equal and therefore $i_{pa}/i_{pc} = 1$ (Wanjau *et al.,* 2015). However, when 'R' is converted further to other products (P), it makes more 'R' to be generated in order to compensate deficiency. This leads to increase in reduction rate and cathodic potential (E_{pc}) becomes more positive resulting to $i_{pa}/i_{pc} \neq 1$ (Bard, 2001).
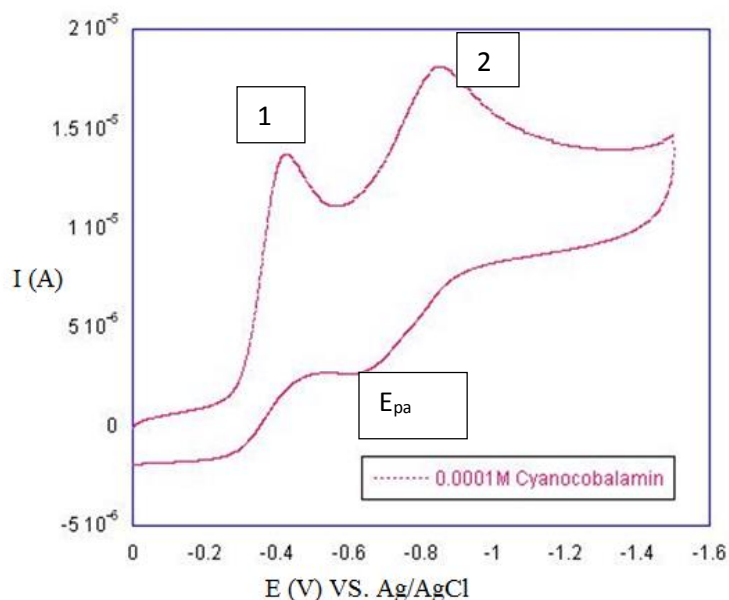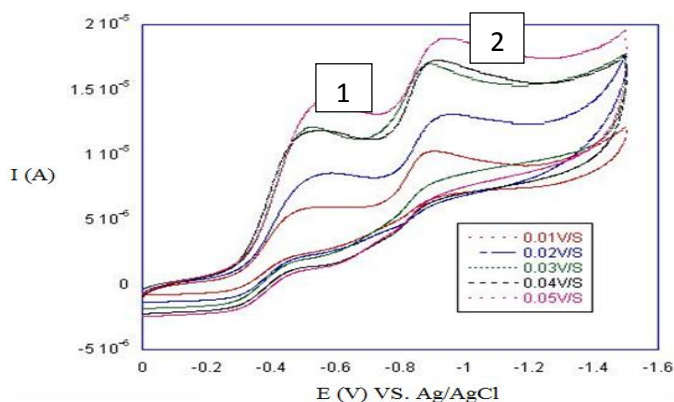

Figure 4.7: Overlay cyclic voltammogram for 0.0001M cyanocobalamin in acetonitrile-water solution containing 0.1M KNO3 at scan rate of 0.03V/s versus Ag/AgCl.

It was found that, the reduction potential and peak current for five waves (Figure 4.7) was - 0.5430 ± 0.023V (peak 1) and - 0.922 ± 0.016 V (peak 2) respectively. These results

obtained compared slightly favorably with - 0.732 ± 0.018 V and - 0.817 ± 0.37 V reported by Wanjau *et al.*, 2015. This is a two-electron reduction process at 298 °K in accordance to the Nernst equation; $E = E^{0'} - (0.059/n) \log Q$, where Q is the reaction quotient, which is the equilibrium expression with initial concentrations rather than equilibrium concentrations, E is the cell potential under non-standard conditions (V), $E^{0'}$ is the cell potential under standard conditions and n is the number of moles of electrons exchanged in the electrochemical reaction. There is supporting report by Lexa, (1976) and Davies *et al.*, 2002 on direct two electron reduction of Co(III) to Co(I) on glassy carbon electrode.

A scatter plot of peak cathodic current versus square root of scan rate, establish a good linear regression between dependent and independent variables (Figure 4.8 and 4.9 respectively).
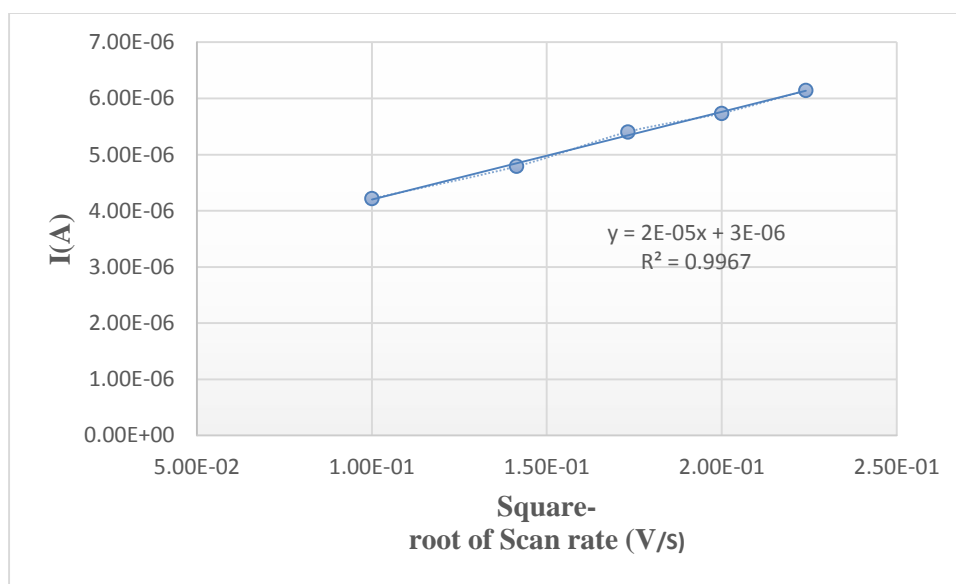

Figure 4.8: The cathodic peak current versus square root of scan rates for 0.0001 M cyanocobalamin in acetonitrile-water in Ag/AgCl electrode.
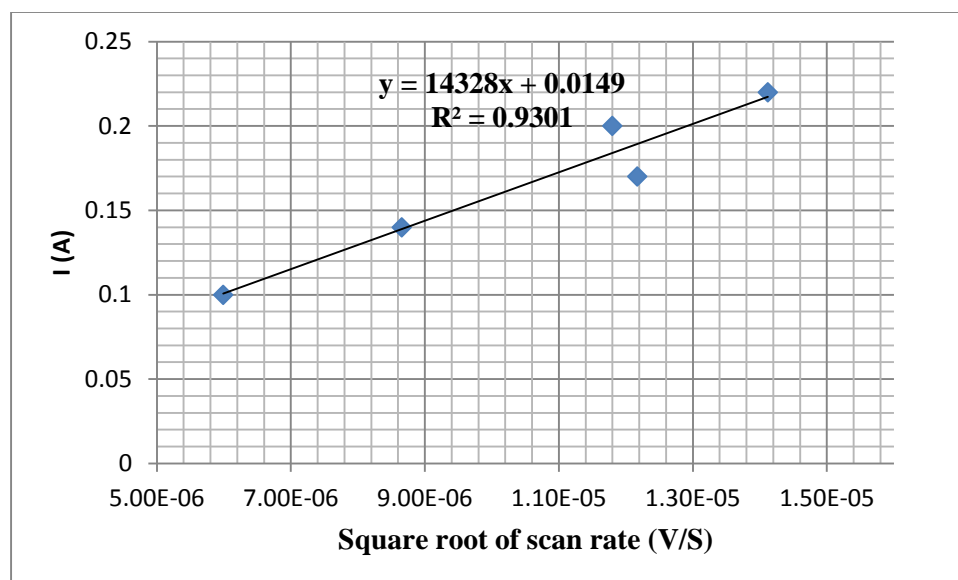
Figure 4.9: The cathodic peak currents versus square root of scan rate for 0.0001 M cyanocobalamin in acetonitrile-water versus Ag/AgCl.

The average diffusion coefficient calculated using Randle-Sevcik equation was found to be 3.4×10^{-7} cm^{2}s^{-1} for peak (1) (Figure 4.8) and 0.8×10^{-8} cm^{2}s^{-1} for peak (2) (Figure 4.9). The current density for cathodic peak (1) was 5.32×10^{-6} A/cm^2 and for peak (2) at 1.05×10^{-5} A/cm^2. The diffusion coefficient (constant) reported for cyanocobalamin from the peak current versus square root scan rate plot for peak (1) is 0.9×10^{-9} cm^{2}s^{-1} (Connors, 1988) and 1.4×10^{-6} cm^{2}s^{-1} (peak 2) all in agreement with the higher viscosity of the ionic liquid media (Schröder, 2000). The experimental value was different from the previous reported values due to change in electrolyte decomposition of the ionic liquid media.

4.1.3. Tetrachlorvinphos in absence of a catalyst

The reduction of 0.003 M Tetrachlorvinphos in acetonitrile-water (v/v 1:1) containing 0.1M KNO$_3$ was studied in absence of Vitamin B$_{12}$. The voltammogram obtained showed a quasi-

reversible Figure 4.10.
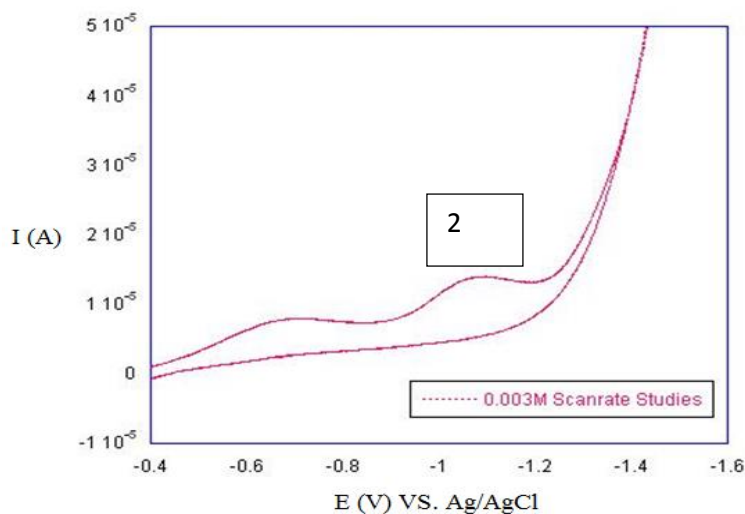
Figure 4.10: Voltammogram for a 3.0 x10^{-3} M tetrachlorvinphos in acetonitrile-water (1:1 v/v) containing 0.1 M KNO$_3$ at 0.01V/s versus Ag/AgCl.

The first (not well-defined) reduction peak was spotted at ~ - 0.710 ± 0.004 V attributing to the two consecutive one-electron reduction of P=O bond of phosphate di-ester group and a second (well defined) reduction peak for five scan rates (Figure 4.11) was found to be around - 1.096 ± 0.029 V versus Ag/AgCl caused by the two consecutive one-electron reduction of C=C bonds. The two peaks observed were irreversible. A previous study by Al-Qasmi *et al.*, 2018 arrayed two irreversible reduction peaks of ~ -1.29 V and ~ -1.35 respectively at 0.1V/s versus Ag/AgCl. The difference would be attributed to substrate concentrations on the electrode surface as well as the solution resistance (Kamau and Rusling, 1985). According to Al-Qasmi *et al.*, 2018, C=C bond occurs at a more negative potential, while P=O bond occurs at potentials more positive than those of C=C bond.
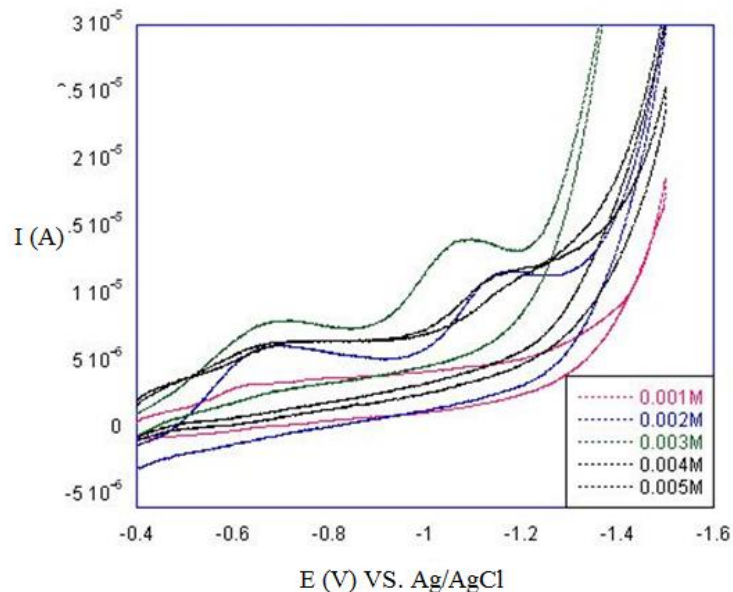
Figure 4.1.1: Overlay cyclic voltammograms for concentration studies of peak cathodic current against peak potential of tetrachlorvinphos.

According to Al-Qasmi (2018), the unprotonated form of tetrachlorvinphos is adsorbed and reduced at the catalytic active site of amalgamated solid silver electrode (Ag-SAE) by two consecutive one-electron transfers, with the initial formation of a radical anion, proton abstraction from the solvent, subsequent reduction of anion followed by rapid protonation in aqueous solution resulting to the C-C saturated bond. The reduction mechanism for the reduction of Tetrachlorvinphos pesticide is shown in **Scheme 1** (appendix B). In this scheme it is proposed that in the tetrachlorvinphos pesticide molecule, the C=C bond is not the only electroactive site, but also the P=O bond of phosphate die-ester group is irreversibly reduced in two consecutive one electron processes.

A plot of cathodic peak (2) current (i_p) is proportional to the square root of the scan rate (Figure 4.13) for scan rate studies. Tetrachlorvinphos is a diffusion controlled process with a diffusion coefficient value of 3.68×10^{-5} cm^{2}s^{-1} and current density of 5.83×10^{-5} A/cm^2.
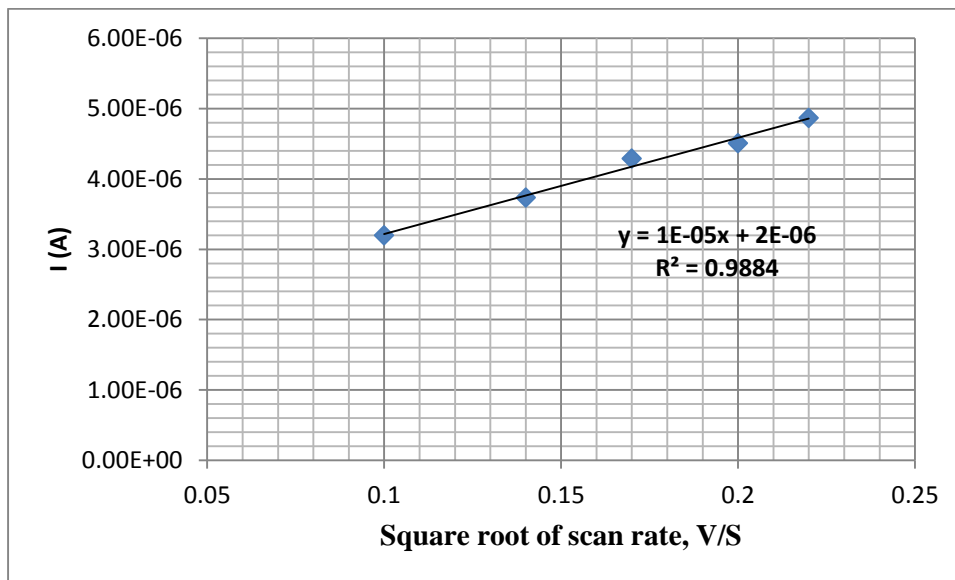
Figure 4.12: A plot of peak (2) cathodic currents versus square root of scan rate (V/s) for 0.001 M tetrachlorvinphos pesticide alone in acetonitrile/water versus Ag/AgCl.

4.1.4. The reduction potential of Tetrachlorvinphos pesticide in the Presence of cyanocobalamin catalyst.

The addition of vitamin B$_{12}$ was found to lower the peak potential from around -1.096 ± 0.029 V to $- 0.923 \pm 0.03$ V versus Ag/AgCl (Figure 4.13). This shows that cyanocobalamin is effective in lowering the reduction potential of tetrachlorvinphos by about 0.168 V.

The diffusion coefficient is 3.37×10^{-5} cm^2s^{-1} and a current density was $2.56 \times 10^{-5}A/cm^2$. This value is lower than the one for tetrachlorvinphos pesticide without a catalyst (- 0. 923 $\pm$ 0.03 V) probably due to increase in the thickness of diffusion layer due to more complexions by catalyst.
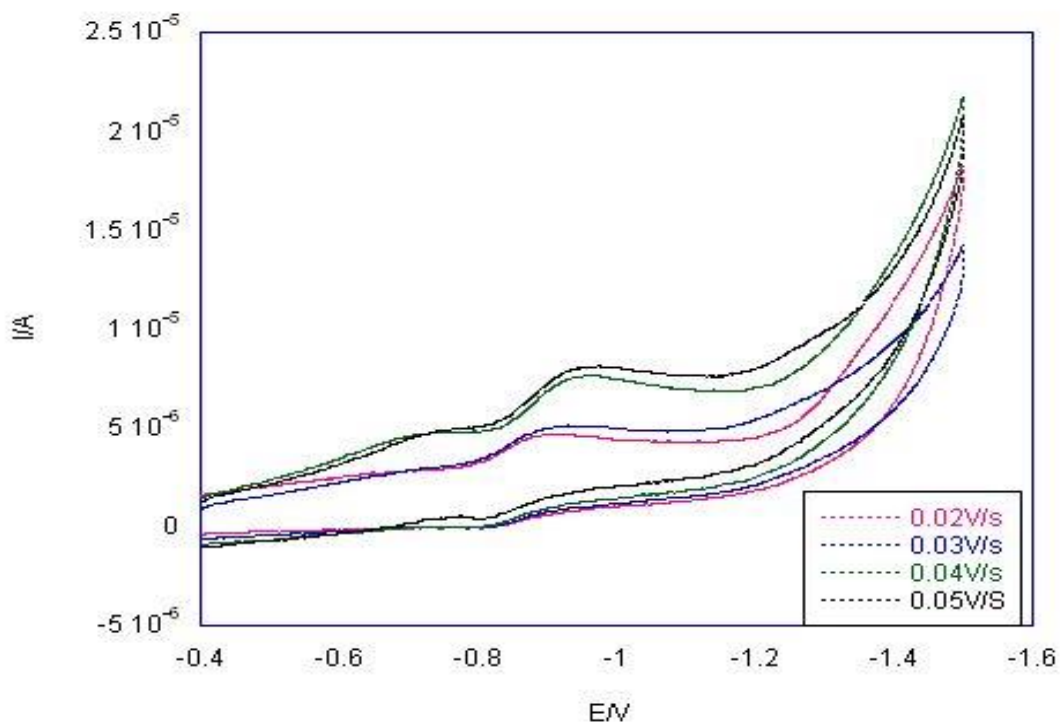
Figure 4.13: Overlay cyclic voltammograms of tetrachlorvinphos in presence of cyanocobalamin at different scan rates.

The reduction of 0.003 M Tetrachlorvinphos pesticide using 1.0×10^{-4} M cyanocobalamin in

acetonitrile-water media is as shown in Figure 4.14.
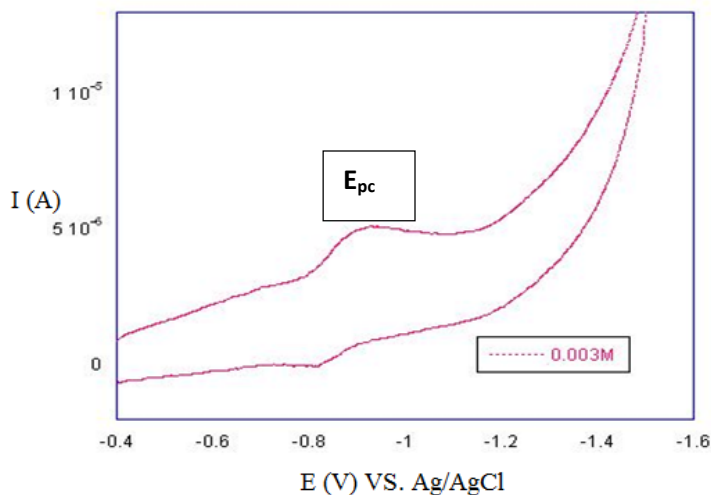
Figure 4.14: Cyclic voltammogram of 3.0×10^{-3} M tetrachlorvinphos pesticide in the presence of 1×10^{-4} M cyanocobalamin catalyst at 0.01V/s versus Ag/AgCl.

Voltammogram overlays for separate reduction of Cyanocobalamin (red), Tetrachlorvinphos

alone (blue) and Tetrachlorvinphos with a catalyst (green) were done as in (Figure 4.15) to

Compare peak potentials.

The reduction peak for tetrachorvinphos (green) is observed at a potential almost coinciding

with the reduction peak potential of Vitamin B_{12} (red). In this case, electrons are donated to

Vitamin B_{12} by the cathode (donor), which reduces the catalyst to the active form. The

reduced catalyst shifts the electrons to Tetrachlorvinphos (acceptor). The reaction occurs at

the formal electrode potential at which the active form of the catalyst is produced. The

product of reduction (Figure 4.14) is unstable and none of it goes through oxidation (Kamau & Rusling, 1992).
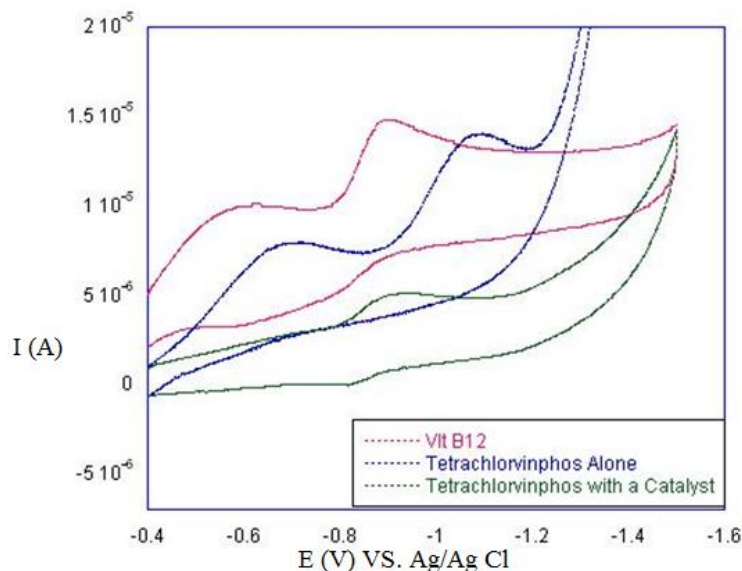
Figure 4.15: Overlay cyclic voltammograms of a: 0.0001M cyanocobalamin (red), 0.001 M tetrachlorvinphos alone (blue) and 0.001M tetrachlorvinphos in presence of cyanocobalamin (green) in acetonitrile-water (1:1 v/v) at 0.01V/s versusAg/AgCl.

The electrochemically generated 'super nucleophile' intermediate, for the case of vitamin B_{12}, the 'super nucleophile' is the Co(I)L complex (Davies *et al*., 2002) is either through equation (i) or (ii) where L is the ligand.

$Co(III)L + e^- \leftrightarrow Co(II)L;$ $Co(II)L + e^- \leftrightarrow Co(I)L$ …………..…………….....(i)

or

$Co(III) L + 2e^- \leftrightarrow Co(I) L$ …………………………………….…(ii)
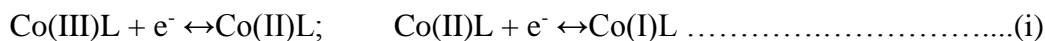
The reduced form of Cyanocobalamin, Co(I), reacts with the organohalides (RX) according to the reaction mechanism in equation (iii) and (iv):

$RX + Co(I)L \rightarrow R\text{-}Co(III)L + X\text{-}$ ……………………………………………(iii)

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$$R\text{-}Co(III)L + (H^{+,}e^{-}) \text{ or } (H\cdot) + CH_2\text{=}CHY \rightarrow R\text{-}CH_2CH_2Y + Co(II)L \quad \ldots\ldots(iv)$$

The above path is catalytic since Co(I)L is regenerated, where L is the macromolecular cyclic portion of a molecule ligand and Y is the electron withdrawing group located at (alpha) α to the carbon–carbon double bond. In the above reaction, rate-limiting step is the attack by Co(I) on alkyl halide. The resulting Carbon-Cobalt bond can be split by visible light, electrolysis, or reducing agents to give carbon-centered radicals that can add to active carbon-carbon double bonds (Davies *et al.*, 2002).

The observable characteristic differences in cathodic peak currents in catalytic or direct at similar substrate concentrations are the most significant features in the reduction process of Tetrachlorvinphos. The peak reduction current (i_p) for the electrocatalysed reduction is not proportional to the square root of the scan rate.

Figure 4.16 indicates a weaker R^2 value of 0.812 derived from Figure 4.13. A strong correlation coefficient is denoted by values ranging from 0.95 to 1.0. This indicates that, the electrocatalysis reaction process (Figure 4.13) is not a diffusion controlled process, hence a quasi-reversible (Muya *et al.,* 2015).

y = 6E-05x - 5E-06
R² = 0.8125
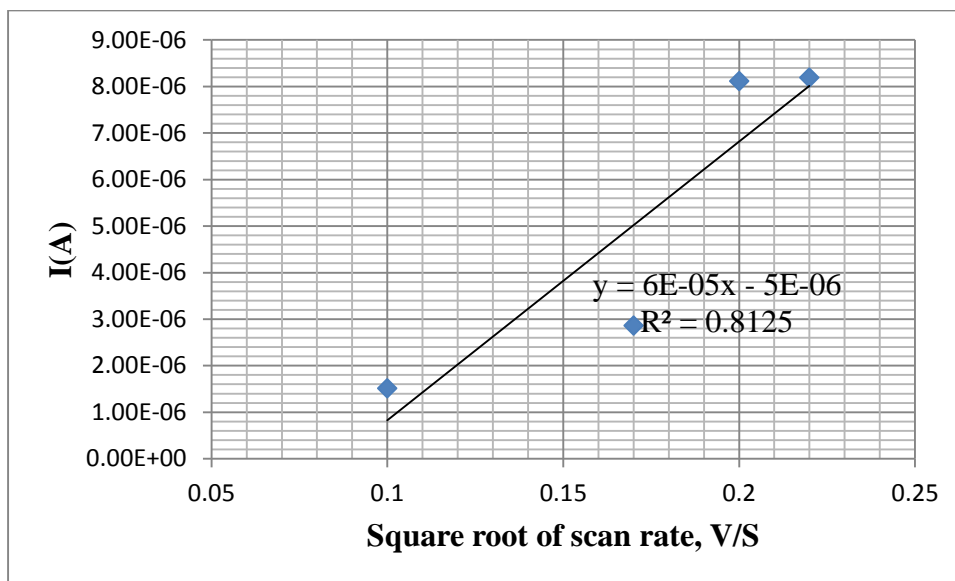
Figure 4.16: A Plot of tetrachlorvinphos with a catalyst peak current against the square root of scan rate.

4.2. UV-Vis Spectrophotometric Method

The spectrophotometric spectrum of cyanocobalamin, tetrachlorvinphos with and without a catalyst obtained are as shown in Figure 4.17, 4.18 and 4.19 respectively. The cyanocobalamin spectrum in acetonitrile-water (1:1 v/v) in 0.1 M KNO_3 exhibited maximum wavelength of absorption within UV region at 360 nm and 549.5 nm respectively. An earlier research done on cyanocobalamin catalyst spectra in aqueous solution exhibited maximum UV and visible region at 278 nm, 361 nm, and 550 nm (Yuan *et al*., 1988). The slight difference observed is due to the change in solvent, temperature, and pH (Ye *et al.,* 2008).
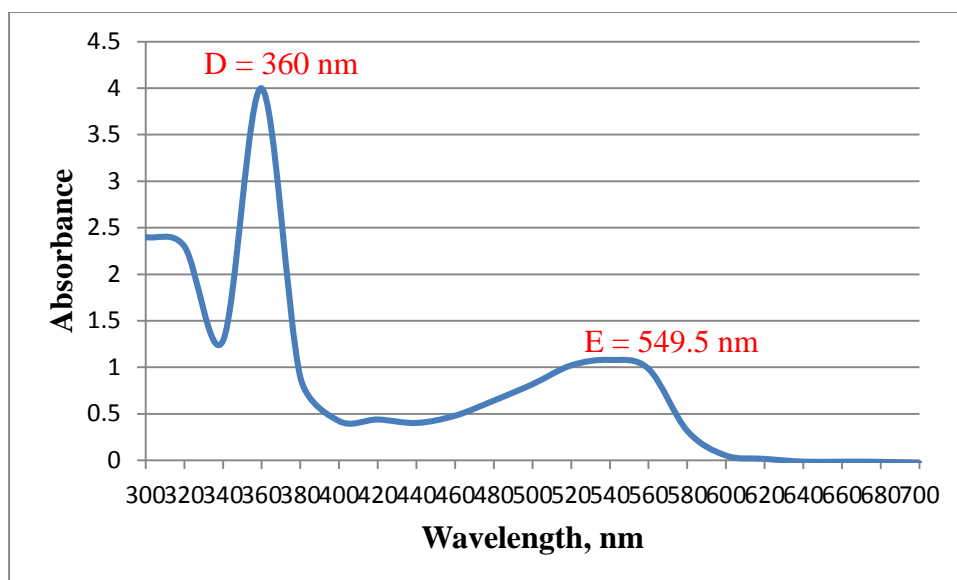
Figure 4.17: UV-Vis spectrum for cyanocobalamin catalyst at scanning range: 300 to 700 nm.
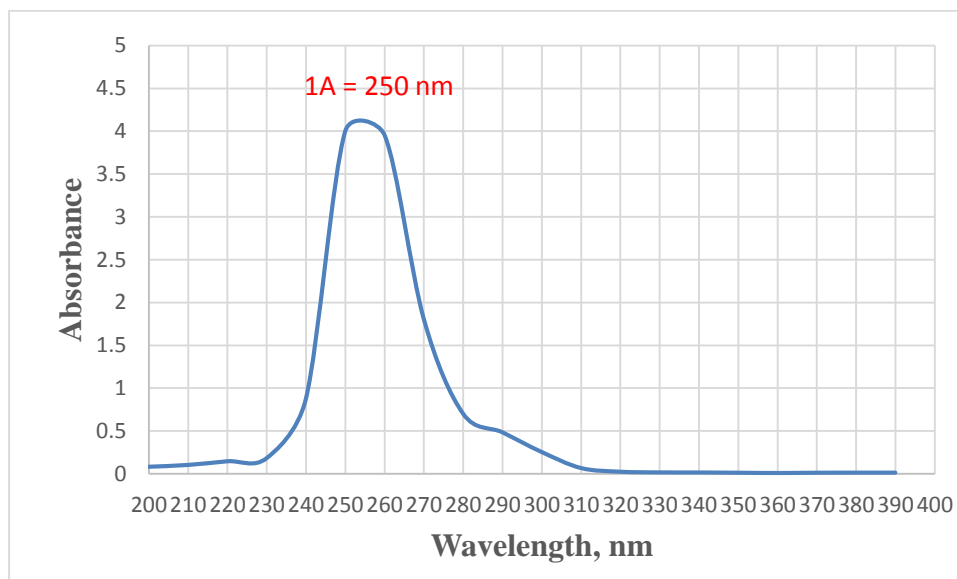
Figure 4.18: UV-Vis spectrum for tetrachlorvinphos pesticide in the absence of a catalyst at scanning range: 200 to 400 nm.

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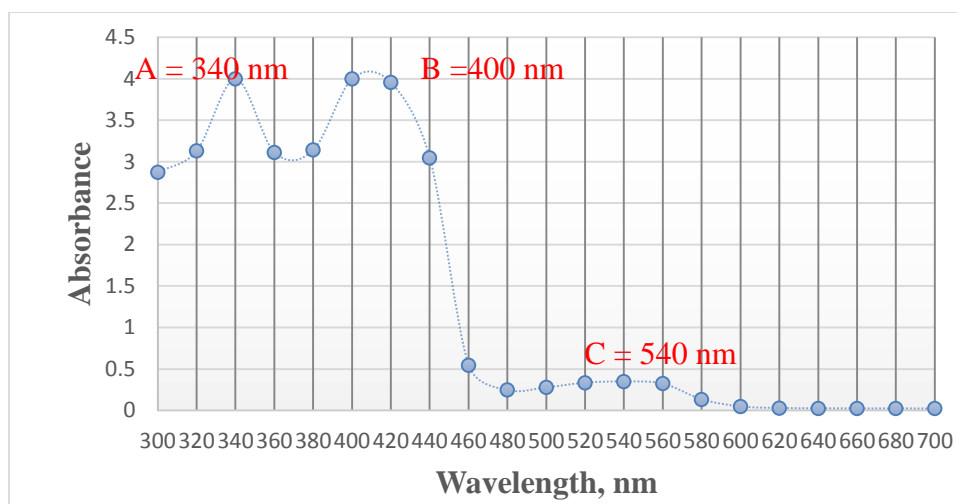
Figure 4.19: UV-Vis Spectrum of tetrachlorvinphos with a catalyst; at scanning range: 300 to 700 nm.

Further studies and analysis were done at these wavelengths using different concentrations. The photometric scan results were used to plot the calibration curve. The calibration curves for tetrachlorvinphos alone and in the presence of a catalyst were obtained by plotting the absorbance versus concentration and are shown in Figure 4.20 and 4.21 respectively.
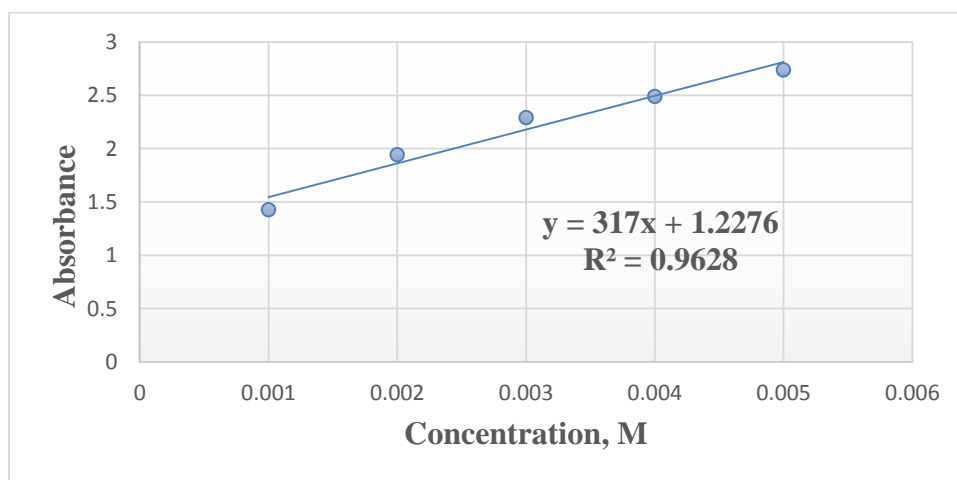
Figure 4.20: Absorbance versus concentration values of tetrachlorvinphos in absence of a catalyst at a wavelength of 250 nm.

Both the calibration curves both (Figure 4.20 and 4.21) obey Beer-Lambert law at dilute concentration range of 0.001 to 0.005 M. The law explains the relationship between concentration and absorbance. The quantity of light absorbed at a particular wavelength is

best explained by a quantity known as molar absorptivity. The quantity ε, is a proportionality constant between absorbance and the product lc. In this experiment, a quartz cuvette of path length 1.0 cm was used to measure the absorbance for 0.002 M tetrachlorvinphos pesticide with and without cyanocobalamin. The maximum wavelength (characteristic value) selected was 250 nm for tetrachlorvinphos pesticide alone and 340 nm for tetrachlorvinphos with a catalyst. The molar absorptivity value was calculated at the maximum wavelength of absorption using Beer-lambert equation ($A = \varepsilon lc$) and found to be 132.5 and 972.5 mol^{-1}cm^{-1}L for tetrachlorvinphos alone and tetrachlorvinphos with a catalyst respectively.
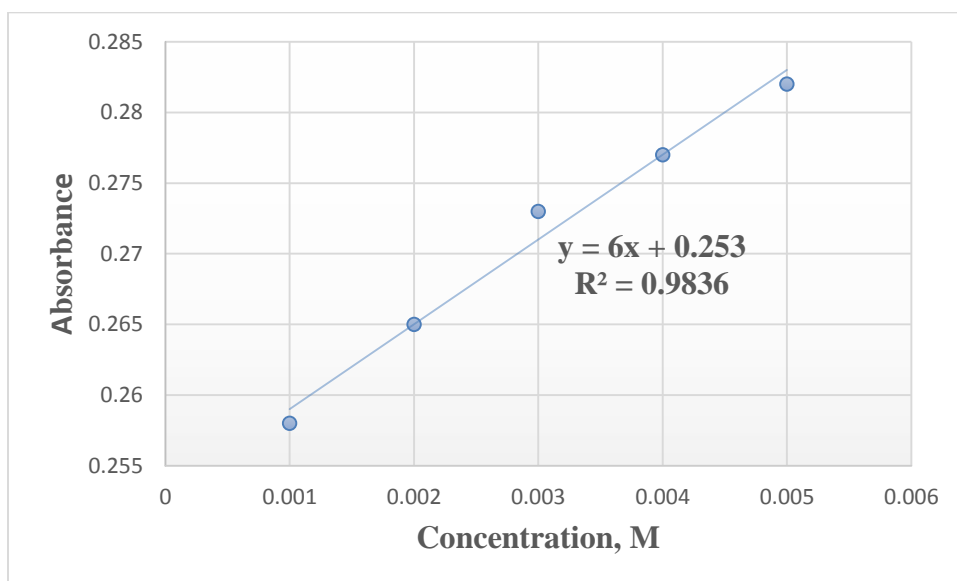
Figure 4.21: Absorbance versus concentration values of tetrachlorvinphos in Presence of a catalyst at a wavelength of 360 nm.

The molecule responsible for light absorption is called a chromophore (Coquelle *et al.,* 2018). In the case of tetrachlorvinphos pesticide, it was found that electron transitions occurred at wavelengths greater than 200 nm and could be associated to $\pi \rightarrow \pi *$ and n $\rightarrow \pi *$ transitions. Tetrachlorvinphos in the presence of a catalyst was found to absorb at a longer wavelength (Figure 4.19) because of increased conjugation due to increase in the number of polynuclear aromatic compounds (fused benzene rings) from cyanocobalamin

(Christian, 2003). Aromatic compounds are good absorbers of UV radiation (Christian, 2003). The Ultraviolet or Visible radiation by metal complex (Cobalt in cyanocobalamin) can also be ascribed to the excitation of the ligand used as an organic chelating agent and complexation with a metal ion (Cobalt) which is similar to protonation of the molecule leading to change in absorption wavelength (Sajan & Birke, 2016). It was also noted that, the addition of a catalyst lead to the appearance of three maximum absorption peaks (Figure 4.19) at wavelengths greater than that of tetrachlorvinphos pesticide in the absence of a catalyst (Figure 4.18).

CHAPTER FIVE

CONCLUSSION AND RECOMMENDATION

5.1. Conclusion

The electrocatalytic reduction of Tetrachlorvinphos occurred at a significantly lower potential with a saving in over potential of about 0.168V compared to direct reduction. The cyclic voltammetry of ferricyanide and tetrachlorvinphos pesticide (in absence of a catalyst) is a diffusion controlled process unlike that of tetraclorvinphos pesticide in the presence of a catalyst. With reference to the UV-Vis studies, it is concluded that tetrachlorvinphos pesticide alone absorbs radiations at single lower wavelength (250.0 nm), while tetrachlorvinphos pesticide with a catalyst absorbs radiation at a multiple wavelength (340.0, 420.0 and 540.0 nm) higher than the latter.

5.2. Recommendation

This study recommends further research to be carried on tetrachlorvinphos in order to identify the decomposition products by Higher Performance Liquid Chromatography (HPLC).

The study also recommends toxicity tests of parent Tetrachlorvinphos Pesticide in comparison with those products of electrocatalytic process.

The study also recommends further work on other organophosphate pollutants such as Ethion and Malathion using other convenient electroanalytical methods such as square-wave voltammetry and rotational-disk voltammetry of study.

Further research is also needed to investigate suitable methods for elimination of these persistent organic pollutant residues in the environment.

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APPENDICES

APPENDIX A: Banned pesticides in Kenya

Source: http://www.pcpb.or.ke/bannedproducts/banned %20pesticides%20in%20kenya.pdf.
Retrieved on June 18, 2018.

	Common name	**Use**	**Year banned**
1	2,4,5 T(2,4,5 – Trichlorophenoxybutyric acid	Herbicide	1986
2	Chlordane	Insecticide	1986
3	Chlordimeform	Insecticide	1986
4	DDT (Dichlor Diphenyl Trichlorethane)	Agriculture	1986
5	Dibromochloropane	Soil Fumigant	1986
6	Endrin	Insecticide	1986
7	Ethylene dibromide	Soil Fumigant	1986
8	Heptachlor	Insecticide	1986
9	Toxaphene (camphechlor)	Insecticide	1986
10	5 Isomers of Hexachlorocyclohehaxne (HCH)	Fungicide	1986
11	Ethyl Parathion	All Insecticide formulations banned except for capsule suspensions	1988
12	Methyl Parathion	Insecticide All formulations banned except for capsule suspensions	1988
13	Captafol	Fungicide	1989
14	Aldrin	Insecticide	2004
15	Benomyl,carbofuran, Thuram combinations	Dustable powder formulations containing a combination of Benomyl Benomyl above 7% carbofuran 10% and Thiram above 15%	2004
16	Binapacryl	Miticide/Fumigant	2004
17	Chlorbenzilate	Miticide	2004
18	Dieldrin	Insecticide	2004

**APPENDIX A: Banned pesticides in Kenya...**

Source: http://www.pcpb.or.ke/bannedproducts/banned %20pesticides%20in%20kenya.pdf.
Retrieved on June 18, 2018.

19	Dinoseb and Dinoseb salts	Herbicide	2004
20	DNOC and its salts (such as ammonium salt, potassium salt and sodium salt)	Insecticide, Fungicide, seed treatment	2004
21	Ethylene dichloride	Fumigant	2004
22	Fluoro acetamide	Rodenticide	2004
23	Hexachlorobenzene (HCB)	Fungicides	2004
24	Mercury compounds	Fungicides,seed treatment	2004
25	Pentachlorphenol	Herbicide	2004
26	Phosphamidon	Insecticide soluble liquid formulati0ns as substanxd that exceed 1000g/L)	2014
27	Monochlotophos	Insecticide/Acaricide	2009
28	All tributylin compounds	All compounds including tributyline oxide, tributylin benzoate,try butyltin fluoride/ tributyltin lineoleate, tributyltin, chloride	2009
29	Atachor	Herbicide	2011
30	Aldicarb	Nematicide/insecticide	2011
31	Endosulfan	Insecticide	2011
32	Lindane	Insecticide	2011

APPENDIX B: Scheme 1.

Reduction mechanism of tetrachlorvinphos on amalgamated solid silver electrode (Al-Qasmi *et al.,* 2018)
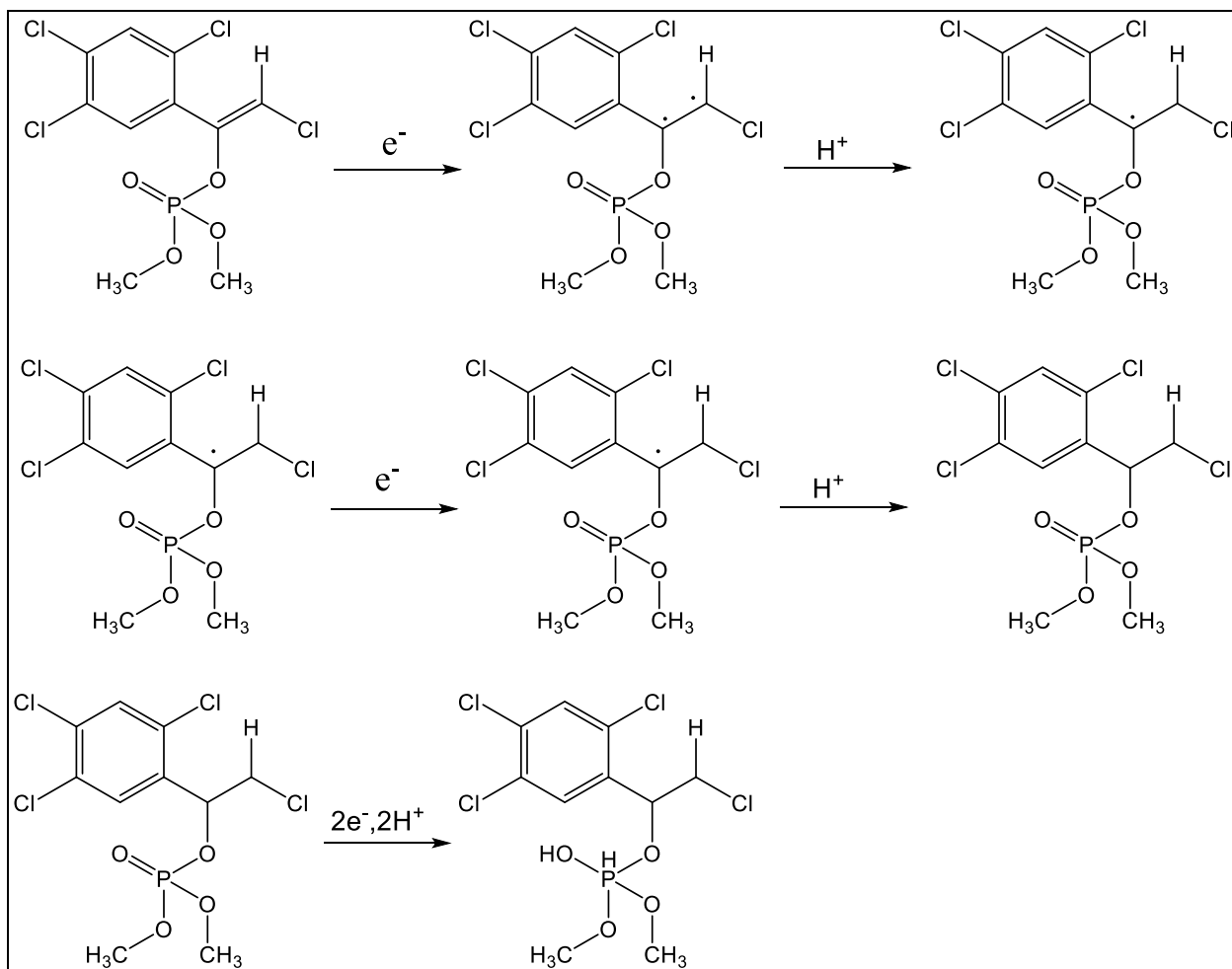
APPENDIX C: Publication of related work

Electrochemical Studies of Potassium Ferricyanide in Acetonitrile-Water Media (1:1) using Cyclic Voltammetry Method

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Abstract

Cyclic Voltammetry is a versatile electroanalytical technique for the study of electroactive species. This method monitors redox behavior of chemical species within a wide range potential. The current at the working electrode is monitored as a triangular excitation potential is applied to the electrode. The resulting voltammograms was analyzed for fundamental information regarding the redox reactions. Cyclic voltammetry are the electrochemical equivalent to the spectra in optical spectroscopy. The number of electrons involved in the redox reaction for a reversible couple is related to the difference in peak potential by 59mV/n. The formal reduction potential is the mean of Peak anodic potential and peak cathodic potential (Epc) and peak anodic current (Epa) and peak cathodic current are close in magnitude. The absolute ratio of peak anodic (ipa) and peak cathodic current (ipc) for both scan rate and concentration studies proved unity for a reversible redox reaction. The mean peak voltage separation value for scan rate and concentration study was found to be 0.0617 and 0.070V respectively. Their standard deviation was found to be ± 0.00493 and ± 0.0003082 respectively. The calculated value for peak voltage for scan rate study and concentration study were found to be slightly higher than the theoretical value of 0.059V/n. The peak anodic current and peak cathodic current versus scan rate graphs and peak anodic current and peak cathodic current versus concentration curves found to exhibit a high R^2 values close to unity at a temperature of 25±1˚C.

Key Words: *Ferricyanide, Cyclic Voltammetry, acetonitrile-water media and Potentiostat.*

1.0 Introduction

Potassium ferricyanide is a bright red salt with a chemical formula $K_3Fe(CN)_6$. The salt contains theoctahedrally coordinated $[Fe (CN)_6]^{3-}$ ion (*Sharpe, 1976*). It is soluble in acetonitrile-water media (1:1) and its solution show some green yellow fluorescence.Like other metal cyanides, solid potassium ferricyanide has a complicated polymeric structure. The polymer consists of octahedral $[Fe(CN)_6]^{3-}$ centers crosslinked with K^+ ions that are bound to the CN ligands (*Figgis,; Gerloch,; Mason,1969*). The K^+---NCFe linkages break when the solid is dissolved in water-acetonitrile media.The $Fe(CN)6^{3-}/ Fe (CN)6^{4-}$ redox couple is used

APPENDIX D: Plagiarism Report

Thesis_Nov 2018_Trimmed for Plagiarism

Submission author:	Zachary Nkunu
Assignment title:	Thesis
Submission title:	Thesis_Nov 2018_Trimmed for Pla...
File name:	Nkunu_Corrected_Thesis_Final_N...
File size:	1.24M
Page count:	53
Word count:	11,079
Character count:	65,804
Submission date:	27-Nov-2018 09:35AM (UTC+0300)
Submission ID:	1045527464

ABSTRACT

This study investigated the electrocatalytic degradation of tetrachlorvinphos pesticide standard in acetonitrile-water media using cynnocobalamin catalyst. It was initiated by reports recorded from various consumers who link their ailment with possibility of pesticide residues in both flora and fauna. Although some studies have been done on electrochemical behavior and rate of degradation of pesticides, no detailed data is available on the same for tetrachlorvinphos pesticide. The study was carried out using cyclic voltammetry and UV-Vis spectrophotometry at a temperature of 24 ± 1 °C. The working electrode potential was concurrently recorded for the resulting current. A preliminary study for cyclic voltammetry was done using a well-known redox couple (Potassium ferricyanide) in order to calibrate the instrument and validate the results. The resulting voltammograms/data were analyzed for fundamental information regarding the redox reactions. For UV-Vis spectrophotometry, absorbance values for substrate were recorded at the maximum absorption wavelengths for various concentrations. The data obtained were analyzed and interpreted using Kaleidagraph software, version 4.1.1 and Microsoft Excel 2010 statistics software. The result shows that tetrachlorvinphos pesticide availed atwo consecutive one-electron reduction peaks, the first (not well-defined) reduction peak at $- - 0.710 \pm 0.004$ V and a second (well defined) reduction peak $- -1.096 \pm 0.029$ V Versus Ag/AgCl. The diffusion coefficient was reported as $3.68 \times 10\text{-}5cm^2s^{-1}$. The current density was 5.83×10^{-2} A/cm². The reduction potential for Tetrachlorvinphos pesticide in the presence of cynnocobalamin catalyst using a glassy carbon electrode was -0.923 ± 0.03 V versus Ag/AgCl with a diffusion coefficient was 3.57×10^{-4} cm²s⁻¹. The current density was 2.56×10^{-2} A/cm². The value for reduction potential of Tetrachlorvinphos pesticide in the two cases resulted to lowering of over-potential by 0.168 Vimplying energy saving. The UV-Vis Spectrophotometer recorded maximum absorption wavelength of Tetrachlorvinphos alone at 250 nm and with a catalyst at (340.0, 400.0 and 540.0) nm respectively. This shows that, electrocatalytic reduction of tetrachlorvinphos pesticide occurred at a significantly lower potential compared to direct reduction with an energy saving of 0.168 V. Cynnocobalamin is a possible suitable catalyst for the degradation of tetrachlorvinphos.

1