UNIVERSITY OF NAIROBI

CONCENTRATION, REDUCTION EFFICANCY AND DEGRADATION OF CHLOROTHALONIL AND LAMBDA CYHALOTHRIN PESTICIDES IN VEGETABLES SOLD IN A NAIROBI CITY MARKET

BY

JAMES MUNGAI

I56/80825/2015

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR AWARD OF THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY OF THE UNIVERSITY OF NAIROBI

AUGUST 2020

DECLARATION

I declare that this research work is my original work and has not been submitted to any institution for any academic award. Where other people's works have been cited, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

SIGN……………………………… DATE……………….............

JAMES MUNGAI

I56/80825/2015

This thesis is submitted for examination with our approval as the university supervisors.

Signature ………………………….. Date ……………………

DR. JOYCE G. N. KITHURE

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NAIROBI

Signature ………………………….. Date ……………………

DR. VINCENT O. MADADI

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NAIROBI

Signature ………………………….. Date ……………………

DR. DEBORAH A. ABONG'O

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NAIROBI

DEDICATION

This research work is dedicated to my inspiration and mentor the late Professor G.N. Kamau for his selfless support, guidance and professional advice during early stages of this study.

ACKNOWLEDGEMENT

In the course of my research work, I have enjoyed inspiration, love, support, guidance and co-operation.

I am very grateful to God for the opportunity He has given to me to undertake this study.

I give special thanks posthumously to the late Prof. G. N. Kamau for his inspiration, professional advice and valuable guidance.

I am very grateful to Dr. Joyce G. N. Kithure, Dr. Vincent O. Madadi and Dr. Deborah A. Abong'o for their professional advice, support, valuable guidance, inspiration and very constructive criticism throughout my research work.

I also extend my gratitude to the PhD students Mr. Mbugua J. K. and Mr. Osoro for there moral and professional support and guidance they accorded to me.

My profound gratitude goes to the technical staff at the Department of Chemistry in particular Alice, Mwangi and Rop for always assisting me during the challenging times and also Mr. Muthoka and Waithera from the Department of Physics for mentoring me to become analytical instrument expert, their Guidance and rich training will forever be useful to me.

My deepest gratitude goes to my Family for their moral support and encouragement throughout the period of this academic endeavor.

ABSTRACT

Vegetables are very essential in almost all the meals served in Kenya and worldwide. Therefore their production is driven by high demands in the Kenyan and the world markets. This pushes the farmers in Kenya to consistently use and sometimes overuse the pesticides so as to produce high yield of vegetables to meet the high demands as well as to maintain the quantity of the vegetables in the markets. This leads to contamination of the vegetables and fruits. Use of pesticides must ensure public food safety as well as safeguard the environment with regard to the chemicals used and their harmful metabolites. The study aimed at determining chlorothalonil and lambda-cyhalothrin pesticides residue levels in spinach, kales and African nightshade sold in Nairobi city park market, effectiveness of washing methods for their removal and their degradation process in the washing solutions. The washing was done using tap water, 0.9% NaCl, 0.1% $NaHCO_3$, 0.001% $KMnO_4$, 0.1% H_2O_2 and 0.1% CH_3COOH. Degradation process of the pesticides was studied by mixing known concentration of the pesticides with the washing solution at ratio of 1:9. The mixture were then subjected to different condition of shaking and settling for different time durations, and then extracted for analysis. UV-Vis spectrophotometer was used for analysis of the pesticide residue levels. The mean chlorothalonil residue levels in spinach, kales and african nightshade were 0.140 ±0.013 mg/kg, 0.100 ±0.007 mg/kg and 0.002 ±0.001 mg/kg respectively. These values were above the maximum residue limits (MRL) of 0.04 mg/kg allowed and also above allowed daily intake (ADI) of 0.02 mg/kg in spinach and kales. The mean lambda cyhalothrin residue levels were found to be 0.034 ±0.003 mg/kg and 0.030 ±0.002 mg/kg in spinach and kales respectively. The concentration of lambda cyhalothrin was below detection limits (BDL) in the african nightshade. The concentrations were below MRL of 0.1ppm and 0.2 in spinach and kales respectively but above ADI of 0.007 mg/kg. 0.001% $KMnO_4$ was the most effective washing solution at 65.67 ±3.73% to 70.23 ±3.82% removal of chlorothalonil and 81.68 ±3.03% to 85.98 ±4.19% for lambda cyhalothrin in all the three vegetables analyzed. Tap water was the least effective pesticides remover, ranging from 10.23 ±2.00% to 11.43 ±0.21% for chlorothalonil and 42.34 ±2.47% to 48.43 ±1.91% removal of lambda cyhalothrin in the three vegetables analyzed. 0.001% $KMnO_4$ gave the highest degradation rate of 86.63 ±0.02% to 89.01 ±1.03% for lambda cyhalothrin and 81.52 ±1.02 % to 84.08 ±1.78% chlorothalonil. Agitation increased the degradation of 0.9% NaCl which surpassed that of both 0.001% $KMnO_4$ and 0.1% CH_3COOH with a degradation of 92.57 ±0.99% of lambda cyhalothrin and 86.97 ±1.36% chlorothalonil after 20 minutes of shaking.

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ABBREVIATIONS AND ACRONYMS

ADI	Allowed daily intake
a.i	active ingredient
ANOVA	Analysis of variance
DDT	Dichlorodiphenyltrichloroethane
dSPE	Dispersive Solid Phase Extraction
EPA	United States of Environmental Protection
ETN	Extension Toxicology Network
FAO	Food and Agriculture Organization
GLC	Gas Liquid Chromatography
Ha	Hectare
HCN	Hydrogen Cyanide
HCDK	Horticultural Crops Directorate of Kenya
HPLC	High Pressure Liquid Chromatography
KARI	Kenya Agriculture Research Institute
KEBS	Kenya Bureau of Standards
KES	Kenya Shillings
KFSSG	Kenya Food Security Steering Group
Kg	Kilograms
mg	milligrams
MoA	Ministry of Agriculture
MRLs	Maximum Residue Limits
MT	Metric Tons
NCPD	National Council for Population and Development
PCPB	Pest Control Products Board
NJDHSS	New Jersey Department of Health and Senior Services
pH	Hydrogen potential (Measure of acidity or alkalinity)
ppm	parts per million
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RSC	Royal Society of Chemistry
SFS	Subjective Facial Sensation
TLC	Thin Layer Chromatography
UV-Vis	Ultra Violet- Visible
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Food security in the world

The population in the world is growing rapidly and projected to increase to between 6.9 billion to 13.1 billion persons by the year 2050 (FAO, 2009; Gerland *et al*., 2014). In addition, about 101 largest cities in the world are home for 757 million people currently, but the population in cities is expected to be 1.13 billion by the year 2050 (Gerland *et al.*, 2014). According to FAO (2009), food production should increase by 70% (FAO, 2009) to feed the increased population. In 2018, the UN- WFP (2018) estimated that 124 million people in 51 countries were facing severe food shortage compared to 108 million people in 48 countries who were food insecure in 2017. The Eastern African countries Uganda, Tanzania, Burundi, Somalia, Kenya as well as Sudan, Ethiopia and South Sudan are among the 51 countries facing the food insecurity. For instance, according to a study by World Bank, 37 countries in sub-Saharan Africa are net food importers (Ng and Aksoy, 2008).

1.2 Food security in Kenya

The population in Kenya was 47.6 million in the year 2019 (KNBS, 2019). This population is growing and is expected to reach 53.7 million by 2020, 66.4 million by 2030 and 91.5 million people by the year 2050 (UN, 2019). This population growth rate remains above Kenya's resources, with large shares of the population exposed to food insecurity, water shortages weather-related disasters and conflicts (NCPD, 2013).

In Kenya food production is already facing challenges due to unpredictable weather patterns, use of outdated technologies, poor soil fertilities, rampant urbanization leading to encroachment of arable land, poor infrastructure and increase in diseases and pests resistant to the pesticides (KARI, 2019). Food security is a major concern for the Kenyan population as noted by Kenya Food Security Steering Group (KFSSG) that most Kenyan lack sufficient and nutritious food to guarantee healthy living standards (KFSSG, 2011). Food insecurity in the country is attributed to factors such as poor food distribution mechanisms; unstructured markets; Low investment in irrigation; over-dependence on a limited number of staple foods;

Low mechanization in food production; Poor post-harvest management and unpredictable rainfall (KFSSG, 2011).

In order to ensure that there is enough food for her population, government of Kenya has embarked on alternative methods of farming such as large scale irrigation schemes as well as mechanization of farming. This calls for use of pesticides mainly insecticides, herbicides and fungicides in large quantities for high food production as well as good quality (Ecobichon, 2001).

1.3 Vegetable farming in Kenya

Vegetables are defined as any part of a plant that is consumed by human as food as part of a savory meal. Some of the plants classified as vegetables which are used as food by human beings include potatoes, beans (i.e. *Phaseolus vulgaris*, *Phaseous coccines, Phaseoulus lunatus*), onions (*Allium cepa, Allium sativum, Allium ampeloprasum*), spinach (*Spinacia oleracea*), cabbages (*Brassica oleracea*), turnip (*Brassica rapa*), carrots (*Dacus carota*) and tomatoes (*Solanum lycopersicum*) (Peel, 2004). In Kenya the most commonly consumed vegetables include; kales, spinach, African nightshade, cabbages, onions, pigweeds, carrots, pumpkin fruit, potatoes, leaf amaranth, pumpkin leaves, sweet pepper, broccoli and tomatoes. Vegetables are made up of cellulose, hemi-cellulose and pectin which give them their texture and firmness (Buren, 1979).

Vegetables provide a good source of vitamins, fibers, protein, energy and essential minerals and related nutrients for human growth and development. The nutrients from the vegetables helps overcoming disorders like anemia, deficiency disorders and other diseases in human beings and therefore considered as “protective supplement food” (Wang *et al.*, 2014).

Vegetable crops have been found to have high medicinal value. Onion and garlic are found to have anti-bacterial property, and have been found to lower the blood sugar in rabbits (Shan, 1989). A study by Unlu *et al.,* (2005) showed that avocados act as a nutrient "booster," allowing the body to significantly absorb more nutrients like alpha-carotene, beta-carotene and lycopene found in fruits and vegetables. Vegetable production is one of the major branches of horticulture and therefore considered as an asset for providing a good source of income to the farmers and they form a vital part of the human diet (Garrow and James, 1993).

In Kenyan household, vegetables are very essential in almost all the meals served and therefore their production is driven by high demands in the Kenyan markets. For the farmers to meet the ever growing demands, they consistently use and sometimes overuse the pesticides so as protect the vegetables from pests, diseases, and weeds which can largely affect the quality and quantity of the yield. Some of pests for vegetables include insects and closely related species including butterflies, weevils, mites and larvae. Many of these pesticides are poisonous to other organisms besides the pests. In addition, the dilemma to farmers is the selection of pesticides, when it must be used, how much should be applied, application frequency and very little knowledge on maximum residue levels for vegetables before they are harvested for consumption or sent to markets. This have led to contamination of vegetables with pesticide residues as reported by various researchers (Kithure *et al.,* 2014, Kumari *et al.,* 2002, 2003 and 2008 Madan *et al.,* 1996).

1.4 Pesticides

Pesticides are defined as any agent intended for prevention, destruction, repulsion or mitigation against of pest a and are divided into groups such as insecticides, acaricides, nematicides, herbicides, avicides, rodeniticides and molluscides depending on the species of the pest targeted (Mathew and August, 1975) . The definition by the FAO International code of conduct on the distribution and use of pesticides is as follows: pesticide is any substance or mixture of substances, meant to prevent, destroy, or control any pest or insect from interfering with production, processing, storage, transfer, or marketing of food, agricultural products and wood (Farrely *et al.,* 1984).

During the early age of farming, salts of metals, sulfur, natural oils, and tobacco products were used as pesticides (Anderson *et al.,* 1981). Chemical synthesis of pesticides has increased considerably. In Kenya in the year 2015 there were more than 985 pesticides registered for crops, about 39 pesticides registered for animals and 123 pesticides registered for use in public health by Pest Control Products Board (PCPB, 2015). The various types of pesticides include; Organochlorines, Organophosphates, Carbamates and Pyrethroids. Pesticides are also classified according to their level of toxicity by World Health Organization (WHO, 2019).

Table 1. 1: The WHO classification of pesticides by hazard and guidelines

Class	**Toxicity**	**Examples**
Class IA	Extremely hazardous	Parathion, Dieldrin
Class IB	Highly hazardous	Eldrin, Dichlorvos
Class II	Moderately hazardous	Lambda-Cyhalothrin, DDT
Class III	Slightly hazardous	Malathion, Chlorothalonil

Source, WHO, 2019

1.4.1 Lambda-cyhalothrin

Lambda-cyhalothrin is a synthetic pyrethroid insecticides and acaricides used to control a wide range of pests in a variety of applications. Pests controlled include aphids, Colorado beetles, thrips, caterpillars and butterfly larvae (RSC, 1991). The crops on which it may be applied include cotton, cereals, ornaments, potatoes and vegetables. The molecular formula is $C_{23}H_{19}ClF_3NO_3$. Lambda cyhalothrin is a colourless solid at room temperature and it is rapidly hydrolyzed under alkaline conditions (FAO/WHO, 1986). The commercials names of the pesticides include Charge, Excaliber, Grenade, Hallmark, Icon and Karate. Figure 1.1 shows the structure of lambda cyhalothrin.

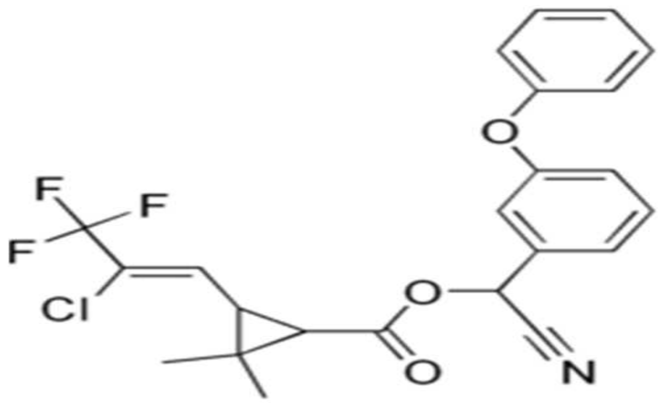

Figure 1. 1: Lambda cyhalothrin structure

Lambda cyhalothrin causes subjective facial sensation (SFS) in people (Hart, 1984) this could be due to Hydrogen cyanide (HCN). Signs of intoxication are characteristic of type II pyrethroid toxicity and include piloerection, subdued behavior, ataxia, unsteady gait, salivation, incontinence, scouring, and chromodacryorrhoea (Nixon and Jackson, 1981). Lambda cyhalothrin residues levels in vegetables should be monitored as well as devise methods of removal of the residues so as to minimize their levels on vegetables before consumption.

1.4.2 Chlorothalonil

This is a fungicide which has been commercially produced since the year 1969 by chlorination of isophthalonitrile or by treatment of tetrachloroisophthaloyl amide with phosphorus oxychloride. Chlorothalonil have a wide spectrum of activity especially in farming where it is used to protect crops such as citrus, currants, berries, bananas, tomatoes, green vegetables, coffee, peanuts, onions and cereals. It is also used in turfs, lawns and ornament plants as well as in wood preservation and in paints (Cox, 1997). The molecular formula is $C_8Cl_4N_2$ and with a molecular mass 265.9 g/mol. Chlorothalonil is a white crystalline solid or powder at room temperature. The trade names for product containing chlorothalonil include Bravo, Daconil, Concord, Echo, Instrata, Termil. In Kenya some of the products include Twiga-Eponil, Twiga-Thalonil and Daconil 720SC. The structure of Chlorothalonil is as shown in Figure 1.2.

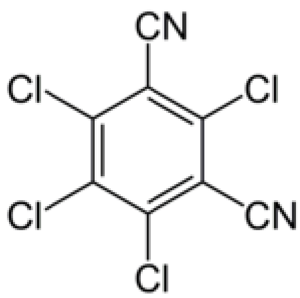

Figure 1. 2: Chlorothalonil structure

Chlorothalonil also has been classified as a probable carcinogen by the United States Environmental Protection- EPA (Scribner *et al.*, 2004). Chlorothalonil is also known to cause irritation to the skin and eyes. Inhaling chlorothalonil causes irritation of the nose, throat and the lungs and therefore causing phlegm (NJDHSS, 1998).

1.5 Statement of the problem

Pesticides are very important in agriculture as they are used to prevent and cure diseases in crops and animals and pests control. This increases the quantity of the yield and improves the quality of the produce both in animals and crops. Despite the many benefits of the pesticides on the farm produce, poor and excess use of pesticides can be dangerous to life due to environmental, soil, and surface water contamination and more so food poisoning by the pesticide residues.

A study by Miller *et al.*, (2004) found that 98% of the sprayed pesticides and 95% of herbicides stray to different targets from the target species including air, water and soil. Toxic residues of these pesticides applied on the vegetables can be injurious to human health, environment, birds, and to the fish (Shan, 1989). Wide use of pentachlorophenol and bromophos methyl cause human risks caused by ingestion of pesticides contaminated foods (Randhawa *et al.*, 2007). When lambda cyhalothrin is ingested or inhaled it may cause severe pulmonary injury, anesthesia, drowsiness, and may aggravate existing chronic respiratory and skin disease (Sharda, 2013)

Kenya largely depends on her agriculture produce for economic growth and to feed her rising population as well as exports to other countries. Therefore pesticide use cannot be abolished since animals and crops need them for high quality production. Inevitably, chemical pesticides are used during the growth process (Li, 2010). At the same time Kenyan populations are exposed to high risk of contaminated vegetables and fruits and with little or no monitoring by the Kenya Bureau of Standards (KEBS) on the Maximum Residue Limits (MRL) levels of the fresh produce sold at the Kenyan markets.

The increased application of pesticides in crop and vegetable farming in Kenya and possibility of high levels of pesticide residue on the vegetables prompted the need to determine and quantify the presence of chlorothalonil and lambda cyhalothrin in spinach, kales and african nightshade sampled from the market and assess the effectiveness of washing methods to reduce the pesticides residues levels before consumption and evaluate the degradation process of the two pesticides in the washing solutions.

1.6 Objectives

1.6.1 General objective

The general objective of this study was to assess the pesticides residues levels in vegetables sold in Nairobi markets, identify the ideal conditions for processing vegetables treated with pesticide and assess degradation process of the pesticides.

1.6.2 Specific objectives

The specific objectives of this study were to:

i. Determine the level of selected in vegetables sold in Nairobi City Markets.
ii. Assess the efficacy of selected solutions to remove pesticides from vegetables.
iii. Determine the most effective solutions for degradation of selected pesticides.

1.7 Justification and the significance of the study

Most of the studies have been done to show how pesticides persist in the environment and the fate of the pesticides in air, soil and water. Studies have also been done on methods for removal of pesticides residues in various vegetables in other parts of the world (Ong *et al*., 1996, Izumi, 1999, Krol *et al*., 2000, Zohair 2001, Adachi and Okano, 2006, Klinhom *et al*., 2008, Ling *et al*., 2011, Gouri *et al*., 2011, Harinathareddy *et al*., 2014). Vegetables sold in Nairobi markets are grown in areas surrounding and within the Nairobi City County. Chlorothalonil and lambda-cyhalothrin pesticides are used concurrently by farmers in Kiambu and kiserian, and other areas which are the main supply of vegetables in Nairobi. Previous studies have shown that vegetables sold in Nairobi are contaminated with heavy metals and pesticide residues (Kutto *et al.*, 2010).

There is need to determine the levels of pesticide residues on vegetables sold in Nairobi City markets, assess the effective washing methods for removal of chlorothalonil and lambda-cyhalothrin residues in spinach, kales and african nightshade and their degradation process in the washing solution with a view to inform the government agencies and the public on the best methods for reducing pesticide residues on fresh vegetables sold in Nairobi and Kenyan markets before consumption.

CHAPTER TWO

LITERATURE REVIEW

2.1 Vegetables sold in Nairobi markets

Vegetables are an important source of food and are highly beneficial to human's health. Essential bio-chemicals and nutrients which are very useful for human bodies are found in vegetables these includes vitamins, carbohydrates, proteins, calcium, carotene, iron ascorbic acid and low concentration of trace minerals (Jimoh and Oladiji, 2005). Vegetables are also a source of revenue for many countries (FAO/WHO, 2008). A study by Hussain *et al* (2001) found out that more than eight hundred million people living in cities and towns around the world were already cultivating crops in vacant plots, marginal lands as well as small private plots. Study conducted by Foeken and Mwangi (2000), in nine African cities revealed that, on average, 35% of the households engaged in some form of agriculture; this was expected to rise beyond 70% depending on their location along the peri-urban to urban transect.

Vegetables are consumed regularly by nearly every household in rural and urban areas in Kenya (Ayieko *et al.,* 2003). The vegetables sold in Nairobi markets come from various areas surrounding Nairobi County. About 50% of the farmers that supply this vegetables use poor farming methods as well as poor quality water to irrigate the vegetables. More than 3700 farmers within a 20 Km radius of Nairobi City center practice irrigation and 36% of them use low quality water (Hide *et al*., 2001). More than 20 million hectares in developing countries are irrigated with poor quality water (Dreschel *et al.,* 2002). The poor quality water can be a source of contamination for vegetables consumed in these areas (Karanja *et al.,* 2010).

A study on kales in Nairobi had indicated the presence of heavy metals, pesticide residues and fertilizers residues levels in the samples (Kutto *et al.,* 2010). A study done by Kithure (2007) indicated that consumers were exposed to significantly high levels of deltamethrin and Lambda cyhalothrin during dry season than during the wet season. The vegetables that were considered in this study include; spinach, kales and african nightshade.

2.1.1 Kales (*Brassica oleracea*)

Kales (*Brassica oleracea*) also commonly known as sukumawiki in Swahili are vegetables that are very good source of minerals and vitamins. It is the most popular leafy vegetables consumed in Kenya. This may be attributed to its short production cycle and high productivity. In 2014, 24,422 Ha of land were used for kales production yielding 348,637MT of kales (HCDK, 2014). They grow very well in well-cultivated soil and limed soil that is less acidic and preferably in manured soils (Larkam, 1976). Figure 2.1 shows kales in a farm.

Figure 2. 1: Kales growing in garden
Source: *Image From http://www.essentiakanan.com/gallery/*

2.1.2 Spinach (*Spinacia oleracea*)

Spinach (*Spinacia oleracea*) is also a very nutritious leafy vegetable which is mostly grown for its edible dark green leaves which are eaten cooked as a vegetable or raw in salads. In 2014, Kiambu and Nyandarua Counties produced 23,239 MT of spinach which accounted for 36.99 percent of the national output (HCDK, 2014). The area under production of spinach increased by 6 percent as the demand for spinach is increasing especially in urban markets in Kenya (HCDK, 2014). Figure 2.2 shows spinach in a farm.

Figure 2. 2: Spinach growing in garden
Source: *Image From http://www.essentiakanan.com/gallery/*

2.1.3 African nightshade (*Solanum nigrum*)

African nightshade (*Solanum nigrum*), commonly known as managu is a leafy vegetable, nutritious and is adapted to the growing conditions of most parts of the country including western and central parts of Kenya. It makes a very important part of the traditional Kenyan and East African diet to balance the calorie-dense maize based staple food. With the increased awareness on the health as well as the nutritional benefits of the african leafy vegetables, the yield of these vegetables increased by 6 percent in 2014, Managu accounted for 17.56 percent of the african leafy vegetables produced in Kenya (HCDK, 2014). Figure 2.3 shows african nightshade growing in a farm.

Figure 2. 3: African nightshade growing in a farm

Source: *Image From http://www.essentiakanan.com/gallery/*

Spinach, kales and african nightshade normally are attacked by the same type of pest which includes; aphids, beetles Colorado and butterfly larvae (RSC, 1991). These pests are usually controlled by pesticides such as Lambda cyhalothrin and Chlorothalonil.

2.2 Pesticide residues

Pesticides are of different chemical class including organochlorine, organophosphate, pyrethroids, carbamates which have human health and environmental effects (Abong'o *et al.*, 2014). In 2010, the pesticides sold by pesticide control board in Kenya were 45% insecticide, 24% herbicide, 21% Fungicide and others were 9% (FAO/WHO, 2010). In Kenya in the year 2015 there were more than 985 pesticides registered for crops, about 39 pesticides registered for animals and 123 pesticides registered for use in public health (PCPB, 2015). Pesticides are used by spraying on the leaves of the vegetables. Leaves are covered with protective cuticles that function by decreasing water loss and protecting the plant from infection by various pathogens. The cuticle is a complex structure consisting of a pectin layer that binds the cutin to the epidermal cell walls and a layer of epicuticular wax on the outside, this structure is known to depend on plant species (Bianchi, 1995). When the stomata are open, gas molecules can diffuse in and out and interact with a large hydrophilic area of water-covered mesophyll cells. Most pesticides are hydrophobic molecules, and thus the large lipid-covered surface of leaves (cuticles) forms an ideal sink for accumulation of pesticides.

2.2.1 Toxicity of pesticides

Pesticides have been associated with harmful effect on human health. The effect ranging from acute such as skin irritation, vomiting, eye irritation, headaches, diarrhea to hazardous impacts such as endocrine disruption, reproduction inhibition and cancer as well as death due to pesticides poisoning (WHO, 1990; WHO, 2010). Some pesticides are highly toxic, non Bio-degradable and persist in the environment for a very long period of time (George *et al.*, 2011). Organophosphate active compounds kill insects by inhibiting *cholinesterase* enzyme in the nervous system (Gallo, *et al*., 1991). *Cholinesterase* enzyme is also found in human and therefore once inhibited the normal ability to respond to external stimuli is destroyed and the human may die of asphyxiation (Calvert *et a*l., 2001).

Bio-accumulation of pesticide residues in human bodies is due to the lipophilic nature of the pesticide (Crinnion, 2009). Certain cancers have been caused by exposure of pesticides through occupational hazards other than that ingested by general population through food (Damalas and Eleftherohorinos, 2011). USA war veterans, who were exposed to sarin and cyclosarin during the destruction of large chemical ammunition caches at Khamisiyah, Iraq during the 1991 Gulf war, were reported to be suffering from neurological and neuropsychiatric disorders (Haley and Kurt, 1997, Proctor *et al.*, 2006). In 1995, 12 people died due to respiratory failure, 47 were totally disabled, and 50 were severely poisoned and about 1000 were moderately poisoned after they were exposed to sarin gas by terrorist in Tokyo subways, Japan (Satoh and Hosokawa, 2000, Yokoyama *et al.,* 1998). Chronic memory and cognitive impairments were also recorded in the victims of the Tokyo subway sarin attack, with 23 of the victims showing chronic memory decline 7 years after the attack (Hatta *et al.,* 1996).

Human intake of toxic substances due to pesticide residues in food commodities can be much higher than intake of these substances related to water consumption and air inhalation (Juraske *et al,*. 2007).

In Kenya 31 pesticides have been banned for use due to their toxicity. They include: Chlordane, chlordimeform, dichlorodiphenyl trichloroethane (DDT), endrin, methyl parathion, captafol, aldrin, ethylene dibromide lindane, endosulfan, alachlor among others. However these banned pesticides find their way illegally in developing countries and are used in the East Africa region for public health vector control leading to contamination of water bodies (Calamari *et al.,* 1995).

2.2.2 Pesticide residues in crops

Studies have shown presence of pesticide residues in different types of crops. Mahugija *et al.* (2017) showed presence of DDT (Dichlorodiphenyl Trichloroethane), DDD (Dichlorodiphenyldichloroethane), endosulfan, chlorpyifos and cypermethrin in onions spinach and cabbages from markets in Dar es Salaam. Cereal grains receive direct application of pesticide in the farm as well as post-harvest treatment and therefore retain a proportion of the pesticide residue on the edible portion delivered to consumers (Seyed and Somashekar, 2010). Whole meal flour obtained from maize grain from Chilchilia, kokwet, kitperis, kunyak and kapkor were found to have high levels of permetrin and malathion residues (Njoroge, 2009). Zelelew, *et al.* (2018) carried out a study in Hadiya zone in Ethiopia which revealed that wheat samples from the farm were contaminated with α-BHC, aldrin, endosulfan and DDT while samples from storages were contaminated with 2,4-D, endosulfan, aldrin and DDT. A study in Nigeria showed cereal grains were contaminated with aldrin mirex,heptachlor epoxide, dichloran, endrin endosulfan, dieldrin, methoxychlor and dichlorodiphenyl-trichloroethane lindane (Ogah *et al.*, 2011). In Poland it was found that 34% of 380 samples of cereals were contaminated with pesticide residues (Neme *et al.,* 2016). Zia *et al.* (2009) found out that, wheat was highly contaminated with pesticides as compared to rice and maize, while the concentration of the pesticide in maize was higher than that in rice, in a study carried out in Pakistan. The active ingredients of these pesticides are persistent and tend to decline slowly. Studies by Gichner (1990) detected pesticide residues on the surface of grains and beans ranging from 16% to 65% of initial levels after 3-9 months of storage.

2.2.3 Pesticide residues in fish

Pesticide residues have been registered in fish. Caldas *et al*. (1999) found out that fish samples from Paranoa Lake of Brasilia in Brazil had organophosphorus residues .A study by Fianko *et al*. (2010) in Densu River basin in Ghana registered high levels of ɣ-HCH, heptachlor, dieldrin, alpha-endosulfan,endosulfan Sulphate and *p,p'*-DDE in fish.

A study by Osei *et al*. (2016) found that organochlorines (aldrin, *p,p'*-DDE and *p,p'*-DDD) and organophosphorus(pirimiphos-methyl and profenofos) in fish from the Tono reservoir. However the levels of all the residues were below the MRL allowed WHO/FAO. Higher concentrations of chlorpyrifos ranging from 0.77 to 2.22µg/g were detected in fish tissues by a study carried out by Akan *et al.* (2014). Samples of fish from lake Naivasha in Kenya were found to have residues of hexachlorocyclohexanes, α- HCH, β-HCH, lindane, cyclodienes and dieldrin (M'Anaimpiu *et al*., 2011). Fish samples from Lake Victoria showed presence of pesticides residues (Madadi, 2005).

2.2.4 Pesticide residues in environment

Surface water contaminated with pesticide residues which is associated with low water quality and exposure of human and wildlife have been detected in streams, rivers and lakes in areas with prolonged use of pesticides (Zhou *et al.,* 2006; Gao *et al.*, 2008; Poolpak, 2008). A study by Hellar (2011) found out that water and bottom-sediments samples from four rivers running through sugar plantations in Kilimanjaro, Tanzania were contaminated with pesticide residues. In river Kikavu the pesticide residues were above the European Union maximum acceptable concentration.

A study carried out between 2008 and 2009 by Njogu (2011) found out that the water and sediment samples from lake Naivasha was contaminated with pesticide residues. Osoro *et al.* (2016) carried out a study that registered presence of organochlorine in water and sediments samples from Rusinga Island. The study detected high concentrations of organochlorine residues in water and sediments samples during dry season while low concentrations were registered during the wet season. Otieno *et al.* (2010) found out that dry soil and water samples from ngare-ndare and ngare sirgoi in isiolo and Ol Ari Nyiro in Laikipia were contaminated with carbofuran and its metabolites. A study carried out on soil from Nyando river catchment in Kenya, showed contamination soil samples by organochlorine pesticide residues for the samples analyzed in the month of February, May, September and December (Abong'o *et al.,* 2015). Further studies have also shown contamination of water and sediments from upper river kuja catchment, Kenya with organochlorine pesticides (Nyaundi *et al.*, 2018).

2.2.5 Pesticides in fruits

According to Nowacka *et al.* (2008) it is nearly impossible to find any samples of fruits such as apples, raspberry and blackcurrant without pesticide residues.

2.2.6 Pesticides in vegetables

Studies have shown presence of pesticide residues in vegetables. A study showed that *telfairia occidentailis* and *celosia argentea* samples purchased from six markets in Lagos state in Nigeria were contaminated with pesticide residues above the allowed limits by WHO of 0.02 mg/Kg (Njoku *et al.*, 2017). A study carried out in Makuyu, Kenya showed that the level of Deltamethrin residues in Kales, Cabbage and Tomatoes were higher during the dry seasons than during the wet seasons. The study further showed that the deltametrin mean residues on the vegetables in dry periods were higher than the ADI of 0.02 mg/kg but below MRLs of 0.2 mg/kg (Kithure *et al.,* 2014).

2.3 Pesticides removal from vegetables

Many pesticide removal methods used in homes have been studied. Chemical recommended for reduction of pesticides are salt, baking soda, distilled vinegar and potassium permanganate (ETN, 1996) Tamarind water and vinegar are among the best suitable solution in removing pesticide residues levels from vegetables and fruits. Studies have revealed that residues of chlorothalonil and tetradifon were successfully removed from commercial eggplant and cucumber with an average removal efficiency of 95% just after 5 minutes of pickling the vegetables in rice-bran paste (Adachi and Okano, 2006). Acidic, alkaline, neutral and ozone solution have also been used in removal of pesticide residues levels from vegetables and fruits (Zohair, 2001). Chlorine solution, ozonated water and strong acid have been proven successful in significantly reducing pesticide residues levels during commercial crop treatment (Ong *et al.,* 1996, Pugliese *et al.*, 2004). Ozone is a strong oxidizing agent hence it is used in drinking and waste water treatment.

Use of ozone for removal of pesticide residues from fruits, vegetables and aqueous solutions under domestic condition is safe. Pesticides such as carbonfuran, phorate, chlorophenylurea, and 2, 4-dichlorophenoxyacetic acid were found to be readily degradable in aqueous ozone solution (Briallas *et al.*, 2003). Chlorine dioxides have been used to reduce pesticide residues on fresh vegetables and fruits (Hwang *et al.*, 2001).

2.4 Degradation process of pesticides

Degradation is the breakdown or decomposition of a substance into other substances. Pesticides degrade through various processes such a photolysis, hydrolysis and microbial metabolism. The formulations contained in pesticides carry the active ingredients, wetting and spreading agents, non- evaporating viscous stickers, humectants and penetrating agents (Hazen, 2000). The additives have hydrophilic and hydrophobic parts that provide medium for photolysis and hydrolysis of pesticides. Lambda cyhalothrin is stable at pH below 8; however under alkaline conditions it hydrolyses through nucleophilic attack of the hydroxyl ion to form a cyanohydrin derivative which degrades to yield hydrogen cyanide (HCN) and the corresponding aldehyde (Gupta *et al.*, 1998). Temperature, pH level and adsorption of the pesticides influences the degradation of the pesticides as found by Barcelo and Durand (1993) who discovered that microbial degradation on alkaline soil is faster than on acidic soils. Chlorine dioxide was used to degrade methiocarb, mancozeb and ethylenethiourea in a study that also revealed the mechanism of the degradation of the three pesticides (Hwang *et al.*, 2003; Tiang *et al.*, 2010).

2.5 Sample extraction and clean up method

QuEChERS is an acronym of quick easy cheap effective rugged and safe method. The method involves extraction of the homogenized crop sample and partitioning using acetonitrile solvent with addition of some salts (magnesium sulphate, sodium chloride and acetate buffer). The extract can then be analyzed directly after centrifugation. The supernatant is further extracted and cleaned using a dispersive solid phase extraction (dSPE) technique. During the process care must be taken to ensure adequate homogenization of the sample. When QuEChERS method is used in analyzing grains such as maize and rice, water must be added during homogenization step and taken into consideration in the final calculations of the spikes and standards concentrations. For liquid-liquid extraction to take place effectively water is required and the water also helps in mixing the maize or rice grains during the homogenization process. QuEChERS is very effective especially in multi-residue extraction and more so when coupled with Gas chromatography and liquid chromatography coupled with mass spectrometry (GC-MS; LC-MS) and/or tandem mass spectrometry (GC-MS/MS; LC-MS/MS) with triple quadruple mass analyzers (Valenzuela *et al.*, 2001)

2.6 Methods of analysis

Pesticides have been analyzed using several methods such as chromatographic techniques like GLC (Nakamura *et al*., 1990), HPLC (Ando *et al*., 1986) and TLC (Jork *et al.*, 1981). Using LC/MS/ and GC/MS have been used to accurately assess the effectiveness of washing and can help to optimize both commercial and in-home washing procedure to minimize pesticide exposure from produce sources(Fadwa *et al.*, 2014) The TLC is much slower than the other chromatographic methods. Other methods include spectrometric, electrochemical methods and enzymatic methods.

In this study Spectrometric method was used in which UV-Vis spectroscopy was used for analysis of measurement at maximum lambda of 227 nm and 232 nm for Lambda-cyhalothrin and chlorothalonil, respectively.

CHAPTER THREE

MATERIALS AND M ETHODS

3.1 Study Area

Nairobi City County is situated at 1º09'S 36º39'E and 1º 27'S 37º06'E and occupies an area of 703.9 Km^2 (272sq mi). Nairobi is 1661 m (5450 ft) above sea level. According to the 2019 census the population of the Nairobi City County was 4.4 million people while the larger Nairobi metropolitan covering an area of 33694.9 Km^2 is estimated to be inhabited by 10.4 million people (KNBS, 2019). Nairobi City County boarders Kiambu county (northern metro), Murang'a County (North Eastern Metro), Kajiado County (southern metro) and Machakos County (Eastern county). The Nairobi City County has several open air markets that sell fresh farm produce like fresh vegetables, fruits, grains and animal products like milk, meat and eggs. These markets include Muthurwa, Kangemi, Kawangware, Marigiti, City park market among others.

3.2 Sample collection, handling and transportation to the laboratory

The Spinach, Kales and African nightshade vegetable samples were bought from City Park Retail market, along Limuru road opposite the Agha Khan University Hospital, in Nairobi County. The sample was collected during the dry season in January; this is because farmers tend to use more pesticides during dry season as compared to wet seasons. The samples were purchased from three of the large scale supplier at the markets. Each vegetable samples consisted of 10kg and were packed in well ventilated plastic bags which were labeled, then temporary stored in polyurethane cool boxes containing dry ice for transportation to the laboratory for extraction and analysis. The samples were stored at 4℃ in the refrigerator in the laboratory before extraction and analysis.

3.3 Reagents and chemicals

All the chemicals and reagents used in this study were of analytical grade, which include: Pesticides analytical standards for chlorothalonil and lambda cyhalothrin were obtained at Aldrich limited (Britain), acetone-analytical grade, glacial acetic acid and acetonitrile HPLC grade from Kobian distributors limited (Nairobi)

Concentrated nitric acid, sodium chloride, distilled deionized water-HPLC grade, potassium permanganate, hydrogen peroxide, sodium hydrogen carbonate and anhydrous magnesium sulphate were purchased from Kobian distributors limited (Nairobi).

3.4 Equipment

U.V-Vis Spectrophotometer (SolidSpec-3700 DUV) instrument from shimadzu Kyoto (Japan) was used for analysis. Analytical balance (ATX224- Shimadu), pH/ORP meter (HANNA-HI 9125), centrifuge (Model 80-2), mechanical shaker (Thermolyne Maxi-Mix III type 65800), and blender (Ramtons) were also used.

3.5 Cleaning of glassware

All the glassware used in the study were washed by soaking in freshly prepared chromic acid for 12 hours and then rinsed with distilled water. Then to remove any adsorbed chromic acid ions, the glassware were soaked in distilled water for 6 hours. The glassware were then dried in oven after rinsing with distilled water.

3.6 Preparation of pesticide standards

The standard solutions of lambda cyhalothrin and chlorothalonil were prepared in analytical grade acetonitrile solution and scanned between the ranges of 200 nm - 400 nm using Shimadzu U.V-Vis Spectrophotometer (SolidSpec-3700 DUV). Pesticide standards were purchased from Aldrich limited (Britain) through Kobian distributors limited (Nairobi). Standard pesticide solution of 100 ppm stock solutions of lambda cyhalothrin and chlorothalonil were prepared in 0.1% acetic acid in acetonitrile. The calibration standard solutions of concentrations 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, and 10 ppm were prepared from the each stock solution by serial dilution for each of the pesticides.

The working standard solutions of the pesticides were prepared from the standard stock solution using the formula:

$C_1V_1 = C_2V_2,$ ………………………………………..Equation 3.1

Where C_1 and V_1 are respectively initial concentration and volume while C_2 and V_2 are respectively the final concentration and volume. A 5 ml of each calibration standard solution was put in 15 ml centrifuge tube and analyzed with UV/Vis spectrophotometer at 227 nm for lambda cyhalothrin and 232 nm for chlorothalonil for calibration curves for the two pesticides respectively. The calibration curve for each of the two pesticides standards was prepared respectively. System suitability was carried out by running 10 ppm, 50 ppm and 100 ppm of lambda cyhalothrin and chlorothalonil standard solutions.

3.7 Limits of detection (LOD) of lambda cyhalothrin and chlorothalonil residues levels

The Limits of detection of lambda cyhalothrin and chlorothalonil were calculated using the formula:

Limit of detection, $y = y_B + 3S_B$ ………………………………………..Equation 3.2

Where y is the limit of detection concentration, y_B is the concentration of the blank and S_B the standard deviation of the blank.

3.8 Recoveries of lambda cyhalothrin and chlorothalonil residues levels in spinach, kales and african nightshade

Spinach, kales and african nightshade from the City Park Retail market, Nairobi were analyzed for the pesticide residue levels. The vegetables were blended using a blender for homogenization; the triplicates of each vegetable samples slurry were weighed 5.0g in 15ml centrifuge tubes then spiked with known concentration of standard solutions of 5 ppm, 10 ppm, 30 ppm and 50 ppm using 1 ml of lambda cyhalothrin and chlorothalonil standard stock solutions. A 5 ml of 1% acetic acid in acetonitrile was added to each of the samples then the tubes were shaken for 1 minute. This was followed by addition of 2 g anhydrous magnesium sulphate ($MgSO_4$) and 0.5 g sodium chloride (NaCl) in each of the centrifuge tubes. The tubes were then shaken for 1 minute and then centrifuged at 3,500 rpm for 5 minutes. The aliquot was filtered through A42 filter paper and analyzed using UV/Vis spectrophotometer using the maximum lambda values for lambda cyhalothrin and chlorothalonil, respectively.

The samples were extracted using the QuECHERS AOAC 2007 method (Anastassiades *et al.*, 2007) without the clean-up step and analysis done to determine the percentage recovery. The percentage recovery was determined using the formula:

$$\% \text{ Recovery} = \left(\frac{\text{spike saple results} - \text{unspiked sample results}}{\text{known concentration of spike added}}\right) \times 100\%$$ ....Equation 3.3

3.9 Sample extraction and analysis of lambda cyhalothrin and chlorothalonil residues levels in spinach, kales and african nightshade

Extraction of the pesticide residues followed QuEChERS AOAC 2007.01 method. The vegetable samples of 50 g of triplicates were separately blended to be homogenized; 5 g of the slurry weighed in a 15 ml centrifuge tube and treated with 5 ml of 1% acetic acid in acetonitrile. The mixture was vigorously shaken for 1 minute, and then 2 g of $MgSO_4$ and 0.5 g of NaCl were added to the mixture and shaken for 1 minute. The solution was centrifuged at 3,500 rpm for 5 minutes for extraction. The aliquot was then filtered and analyzed using UV-Vis spectrophotometer using the maximum lambda values for Lambda cyhalothrin and Chlorothalonil respectively and the concentrations of the pesticide residues levels in each vegetable was recorded.

3.10 Preparation of washing solutions

Distilled water was used as a diluent and the washing solutions were freshly prepared as follows:

3.10.1 Preparation of 0.9% NaCl (% w/v)

A 0.9% NaCl solution was prepared by accurately measuring 9.00g on the analytical balance and dissolved in 250 cm^3 distilled deionized water in a 1,000 cm^3 volumetric flask, and the solution made up to the mark.

3.10.2 Preparation of 0.1% $NaHCO_3$ (% w/v)

A 0.1% $NaHCO_3$ solution was prepared by measuring 1.00 g of $NaHCO_3$ using analytical balance and dissolved in 250 cm^3 distilled deionized water. The solution was diluted to the mark in a 1 litre volumetric flask.

3.10.3 Preparation of 0.1% Acetic acid (% v/v)

A 1 cm^3 of glacial acetic acid was measured and dissolved in 250 cm^3 distilled deionized water in a 1000 cm^3 volumetric flask. The solution was then made up to the mark.

3.10.4 Preparation of 0.001% $KMnO_4$ (% w/v)

A 0.001% $KMnO_4$ solution was prepared by measuring 0.01 g of $KMnO_4$ using analytical balance. The 0.01 g of $KMnO_4$ was the dissolved in 250 ml and made up to 1,000 ml using a volumetric flask.

3.10.5 Preparation of 0.1% H_2O_2 (% w/v)

A 0.1% H_2O_2 was prepared by measuring 3.30cm^3 of 30% hydrogen peroxide stock solution and dissolved in 250 cm^3 distilled deionized water in a 1,000 cm^3 volumetric flask, and the solution was then made up to the mark.

3.10.6 Preparation of tap water

Tap water was used as collected from the tap with no pretreatment and was used as a control for the washing solution.

3.11 Washing pesticides from vegetables

Each type of the three vegetable samples was divided equally into 39 sub samples of about 50 g. Triplicate sub samples from each division was extracted and analyzed while the remaining 36 sub samples sprayed with 100 ml of 40 ppm lambda cyhalothrin and chlorothalonil solution for 1 min to simulate the adsorption of pesticides in the vegetables. The sprayed samples were then air-dried for 1 hour in the shade. The pesticide-treated samples were then soaked in 500 ml of each six washing solution for 20 min, with the initial 1 minute gentle rotation by hand to mimic washing procedure done in household vegetable washing. After the washing process, the washed vegetable samples were air dried for 1 hour in the shade, homogenized and pesticides extracted. The aliquot were filtered using A42 filter paper and analyzed using UV/Vis spectrophotometer using the maximum lambda values for Lambda cyhalothrin and Chlorothalonil, respectively, and the concentrations of the pesticide residues levels in each vegetable recorded.

3.12 Degradation of pesticides in the washing solutions

This study focused on the degradation of chlorothalonil and lambda cyhalothrin in the washing solutions at room temperature, agitation of the mixture of pesticide standard and washing solution and at pH values of 3.82±0.07, 6.67±0.09 and 7.12±0.64 for 0.1% CH_3COOH, 0.9% NaCl, and 0.001% $KMnO_4$ solutions, respectively.

This was done by preparing 40 ppm of chlorothalonil and lambda cyhalothrin solutions in water as per the manufacture's recommendation. 40 mg active ingredient (a.i) of lambda cyhalothrin was accurately weighed and dissolved in 250 ml distilled deionized water in a 1,000 ml volumetric flask. The solution was then made up to 1,000 ml to make 40 ppm solution of lambda cyhalothrin. To prepare 40 ppm chlorothalonil, 55.55 µl containing 40 mg active ingredient (a.i) of chlorothalonil was measured using a micro-litre syringe and dissolved in a 250 ml distilled deionized water. The solution was then made up to 1,000 ml in a volumetric flask.

A sample of 5 ml of 40 ppm lambda cyhalothrin and 40 ppm chlorothalonil pesticide solutions were then mixed separately with 45 ml of each of the three washing solutions (0.9% NaCl, 0.1% CH_3COOH and 0.001% $KMnO_4$) in ratios of 1:9. The first set of the mixtures were then allowed to settle for varying time (5, 15, 30, 45 and 60 minutes). The resulting solution were extracted for the pesticide residue and analyzed for chlorothalonil and lambda cyhalothrin levels using UV-Vis spectrophotometer.

The half-life of lambda cyhalothrin and chlorothalonil will be determined using the formula;

$$t½ = \frac{-0.693}{-k}$$

Where t½ is the time taken for the initial concentration to degrade to half concentration and k is the rate constant for the first order kinetics.

Regression analysis was used to determine the value of k, assuming that the degradation of lambda cyhalothrin and chlorothalonil follows the first order kinetic, using the formula;

$$\ln\left(\frac{C}{Co}\right) = -kt$$

Where C is the concentration of lambda cyhalothrin and chlorothalonil standard at time t, C_o is the concentration of lambda cyhalothrin and chlorothalonil standard at time t=0 and k is the first order rate constant.

3.13 Degradation of pesticide standards in different washing solutions under varying settling time

The second set of mixtures of 40 ppm lambda cyhalothrin and 40 ppm chlorothalonil pesticide solutions and different washing solutions (0.1% CH_3COOH, 0.9% NaCl, and 0.001% $KMnO_4$) at a ratio of 1:9 were subjected to a constant shaking time of 5 minutes on a mechanical shaker then allowed to settle for different durations of time 0, 10, 20, 30, 40, 50 and 60 minutes. The resulting solution were extracted and analyzed for chlorothalonil and lambda cyhalothrin pesticide residue levels using UV-Vis spectrophotometer.

3.14 Degradation of pesticide standards solutions in different washing solutions under varying shaking time

The third set of mixtures of 40 ppm lambda cyhalothrin and 40 ppm chlorothalonil pesticide solutions set of mixtures of pesticide and different washing solutions (0.1% CH_3COOH, 0.9% NaCl, and 0.001% $KMnO_4$) at a ratio of 1:9 were shaken on a mechanical shaker for different duration of time of 0, 5, 10, 15 and 20 minutes then allowed to settle for a constant period of time 20 minutes. The resulting solutions were then extracted and analyzed for the chlorothalonil and lambda cyhalothrin pesticide residue levels using UV-Vis spectrophotometer.

3.15 Data analysis

Minitab and Microsoft excel software was used for analyzing the data obtained. Descriptive statistics was used to calculate the mean and standard deviations of the data obtained. Tables, charts and graphs were used to present the data. One way ANOVA (Analysis of Variances) was used to test the variation of the concentration of the pesticide residues levels under different shaking conditions.

CHAPTER FOUR

RESULTS AND DISCUSSION

The results obtained for the analysis of lambda cyhalothrin and chlorothalonil pesticide residues levels in spinach, kales and african nightshade sold in Nairobi City markets, the effectiveness of removal and degradation process in different washing solutions are discussed in this chapter. The values are shown as a mean ± SD.

4.1 Calibration of U.V-Vis Spectrophotometer for analysis of lambda cyhalothrin and chlorothalonil

The results for calibration curves for absorbance against concentration for lambda cyhalothrin at 227 nm and chlorothalonil at 232 nm were obtained and they obeyed the Beers' law; as shown in Figure 4.1 and 4.2 and Figures 4a and 4b appendix for lambda cyhalothrin and chlorothalonil, while the scan range were respectively.

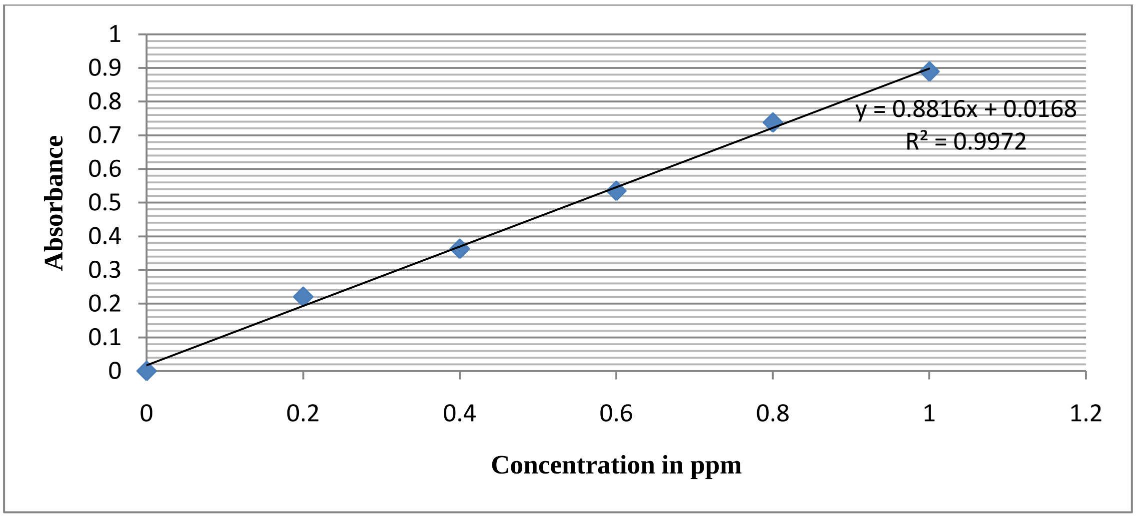

Figure 4. 1: The calibration curve for lambda cyhalothrin using UV/Vis

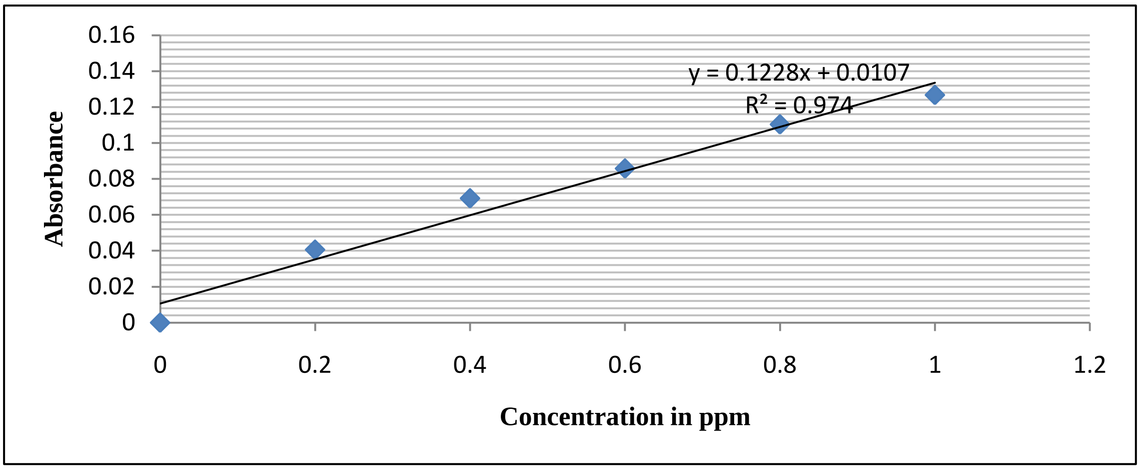

Figure 4. 2: The calibration curve for chlorothalonil using UV/Vis

The linearity of each calibration curves was determined from regression equation (Table 4.1) the values were above 0.97, hence considered suitable for use in determining the concentration of lambda cyhalothrin and chlorothalonil residues in the vegetables. The linear equations as shown in Table 4.1

Table 4. 1: Regression equations for the calibration curves

Pesticide	Linear equation	Regression
Lambda cyhalothrin	y = 0.8816x + 0.0168	$R^2 = 0.997$
Chlorothalonil	y = 0.1228x + 0.0107	$R^2 = 0.974$

4.2 Limits of detection for lambda cyhalothrin and chlorothalonil using U.V-Vis spectrophotometer

The distilled water was used the blank in this study. The data obtained on analysis of the blank using the UV-Vis spectrophotometer were used to determine values of the limits of detection for lambda cyhalothrin and chlorothalonil which were as shown in Table 4.2. These results were used to determine the presence of the pesticide residues in all the samples and any values that were below these were considered to be below the detection limits and treated as such.

Table 4. 2: Limits of detection for lambda cyhalothrin and chlorothalonil

Pesticide	Limit of Detection (mg/Kg)
Lambda cyhalothrin	0.004
Chlorothalonil	0.001

4.3 Percentage recovery for lambda cyhalothrin and chlorothalonil pesticides in the vegetables

Method validation included analysis of recovery samples which was carried out using; spinach, kales and african nightshade. The samples were spiked with 5 ppm, 10 ppm, 30 ppm and 50 ppm of lambda cyhalothrin and chlorothalonil standards solutions, respectively. chlorothalonil had higher recovery for all the three vegetables (Table 4.3) compared to the lambda cyhalothrin. Higher recoveries were also registered from spinach and kales. The pesticides residue levels detected in spinach, kales and african nightshade were not corrected for matrix effects, because all recoveries were within acceptable range fell within the accepted range of 70 to 120% (Hill, 2000). Table 4.3

Table 4. 3: Percentage recoveries of pesticide residue levels in spinach, kales and african nightshade vegetables

Percentage recoveries of chlorothalonil pesticide in vegetables			
Level spiked (ppm)	**African nightshade**	**Spinach**	**Kales**
5	76.45±4.50	92.23 ±2.30	88.98±4.20
10	78.45±1.10	92.76 ±2.70	87.73±0.30
30	78.12±5.00	94.59 ±3.00	89.19±2.42
50	80.86±1.30	93.75 ±2.10	88.85±3.31
Percentage recoveries of Lambda cyhalothrin in vegetables			
5	73.74±1.90	89.56±3.13	84.76±0.67
10	75.45±0.60	89.01±1.00	86.01±0.56
30	75.01±2.80	90.32±5.70	86.67±1.70
50	75.79±4.50	91.02±1.40	86.60±0.91

n=3, mean ± standard deviation

4.4 Pesticide residue levels in spinach, kales and african nightshade sold in city park market in Nairobi city

Level of lambda cyhalothrin residues in spinach, kales and african nightshade vegetable samples purchased from city park market along the Limuru road are shown in Table 4.4

Table 4. 4: Pesticide residue levels in spinach, kales and african nightshade sold in City Park Market in Nairobi

Vegetables	Lambda cyhalothrin (mg/Kg)	MRL	Chlorothalonil (mg/Kg)	MRL
African nightshade	BDL	0.200	0.002± 0.001	0.040
Spinach	0.034 ± 0.003	0.100	0.140 ± 0.013	0.040
Kales	0.030 ± 0.002	0.200	0.100 ± 0.007	0.040

n=3, BDL- Below the detection limits, MRL- maximum residue limits, mean ± standard deviation.

From Table 4.4 the data shows that spinach had the highest pesticide residue levels with a mean of 0.034 ±0.003 mg/Kg for lambda cyhalothrin and 0.140 ±0.013 mg/Kg for chlorothalonil respectively. Kales registered 0.030 ±0.002 mg/Kg and 0.100 ±0.007 mg/Kg for lambda cyhalothrin and chlorothalonil, respectively. Lambda cyhalothrin was not detected in african nightshade; however chlorothalonil was detected at 0.002 ±0.001 mg/Kg. The presence of lambda cyhalothrin and chlorothalonil in the vegetables means that the pesticides were being used at the same time. The levels of pesticide contamination in the vegetables is consistence with values reported by Kithure (2007) that found lambda cyhalothrin in kales sold in Makuyu, Murang'a County at a concentration of 0.03 ±0.01 mg/Kg during dry seasons. A study by Mbugua (2015), found out that vegetable grown in organic farm in Kikuyu, Kiambu County contained 0.12 mg/Kg of chlorothalonil and 0.04 mg/Kg of lambda cyhalothrin in spinach. A study carried in Cotonou and Parakou cities in Benin found out that vegetables contained lambda cyhalothrin ranging from 0.12mg/Kg to 0.18mg/Kg and 0.002mg/Kg in cabbages and lettuce respectively (Djouaka *et al.*, 2018). In this study, the residue levels lambda cyhalothrin obtained in the vegetable samples were below the MRL while the levels of chlorothalonil were above the MRL. However the residue levels of both chlorothalonil and lambda cyhalothrin were above the ADI levels apart from that of chlorothalonil in african nightshade.

4.5 Removal of chlorothalonil and lambda cyhalothrin by different washing solutions

The effectiveness of different methods to remove pesticide residues from vegetables was determined by first spiking the vegetables with 40 ppm lambda cyhalothrin and chlorothalonil separately. The dried samples were washed with tap water, 0.9% NaCl, 0.1% $NaHCO_3$, 0.1% H_2O_2, 0.1% CH_3COOH, 0.001% $KMnO_4$ separately. The percentage amount of the pesticide residues removed were determined by comparing the initial amount of pesticide spiked on the vegetable washed and the subsequent amounts after washing. In addition the amount of pesticide residues remaining on unwashed vegetables were also determined for comparison. The results obtained are shown in the Appendix II.

Tap water removed the least amount of the pesticide residue from all the vegetables (Appendix II), ranging from 10.23 ±2.00% to 11.43 ±0.21% for chlorothalonil and 42.34 ±2.47% to 48.43 ±1.91% for Lambda cyhalothrin. 0.001% $KMnO_4$ removed the highest amount of the residues from all the vegetables ranging from 65.67 ±3.73% to 70.23 ±3.82% for chlorothalonil and 81.68 ±3.03% to 85.98 ±4.19% for lambda cyhalothrin. This can be attributed to oxidizing ability of the $KMnO_4$. 0.1% H_2O_2 also registered a high ability in removal of the pesticides ranging from 60.76 ±3.01% to 65.46 ±1.75% of chlorothalonil and 74.78 ±2.78% to79.97 ±3.28% of lambda cyhalothrin. This is also attributed to the oxidizing ability of the H_2O_2. This results agrees with earlier study that indicated that washing samples with 0.001% $KMnO_4$ was most effective as compared to other washing solutions and water the least effective (Gouri *et al.*, 2011).

The data from Appendix II were plotted and are shown in Figure 4.3 for removal of chlorothalonil and Figure 4.4 for lambda cyhalothrin, respectively

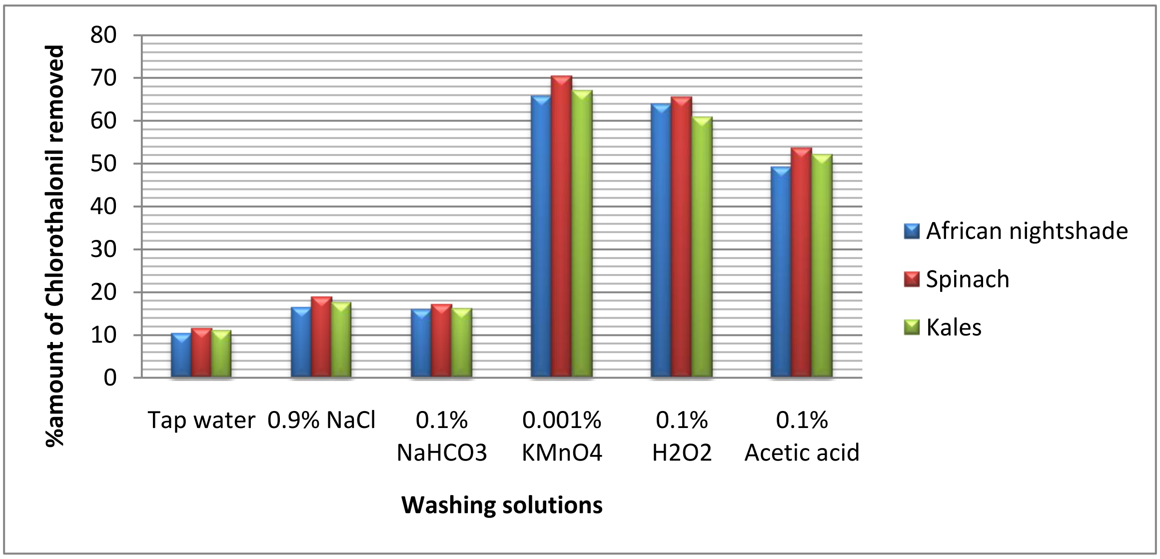

Figure 4. 3: Effectiveness of washing solutions on removal of chlorothalonil residue levels in african nightshade, spinach and kales vegetables

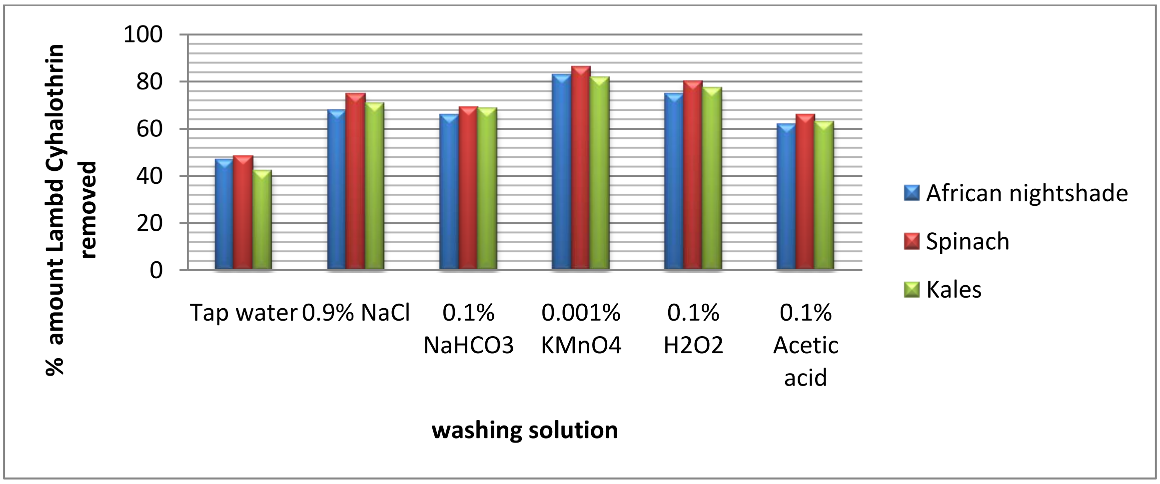

Figure 4. 4: Effectiveness of washing solutions in removal of lambda cyhalothrin residue levels in african nightshade, spinach and kales vegetables

African nightshade registered the lowest levels of removal ranging from 10.23 ±2.00% to 65.67 ±3.73% and 46.76 ±2.67% to 82.97 ±1.63% of chlorothalonil and lambda cyhalothrin residues respectively (Appendix II; Figure 4.3 and Figure 4.4). The low levels of removal from african nightshade may be attributed to leaves size and nature which were relatively smaller in surface area and not waxy. The amount of the pesticide residue remaining in african nightshade samples after washing with 0.001% $KMnO_4$ was 6.78 ±0.57mg/kg and 2.80 ±0.16 mg/kg of chlorothalonil and lambda cyhalothrin respectively. While the amount left after washing with water was the highest at 17.16 ±0.38 mg/kg and 8.78±0.33 mg/kg of chlorothalonil and lambda cyhalothrin respectively. (Appendix II; Figure 4.5 and Figure 4.6)

The removal of the both chlorothalonil and lambda cyhalothrin residues using the washing solutions was more effective on the spinach ranging from 11.43 ±0.21% to 70.23 ±3.82% chlorothalonil removal, lambda cyhalothrin removal was also highly effective on spinach ranging from 48.43 ±1.91% to 85.98 ±4.19% (Appendix II; Figure 4.3 and Figure 4.4). This may be attributed to the nature and size of the spinach leaves which have relatively large surface area and not waxy. The amount of the pesticide residue remaining in spinach samples after washing with 0.001% $KMnO_4$ was 7.10 ±0.71 mg/kg and 2.76 ±0.78 mg/kg of chlorothalonil and lambda cyhalothrin respectively. While the amount left after washing with water was the highest at 21.14 ±0.47 mg/kg and 10.15 ±0.39 mg/kg of chlorothalonil and lambda cyhalothrin respectively (Appendix II; Figure 4.5 and Figure 4.6). These levels were relatively higher than the MRL of 0.04mg/kg and 0.1 mg/kg of chlorothalonil and lambda cyhalothrin respectively, allowed by WHO in spinach (FAO/WHO 1996).

In kales 10.90 ±1.09% to 67.06 ±2.04% of chlorothalonil and 42.34 ±2.47% to 81.68 ±3.03% of lambda cyhalothrin was removed by the washing solutions. Kales had large waxy leaves as compared with the other vegetables types (Appendix II; Figure 4.3 and Figure 4.4). The amount of the pesticide residue remaining in kales samples after washing with 0.001% $KMnO_4$ was 6.97 ±0.42 mg/kg and 3.17 ±0.52 mg/kg of chlorothalonil and lambda cyhalothrin respectively. While the amount left after washing with water was the highest at 18.86 ±0.21 mg/kg and 9.99±0.34 mg/kg of chlorothalonil and lambda cyhalothrin respectively (Appendix II; Figure 4.5 and Figure 4.6). These levels were relatively higher than the MRL of 0.04mg/kg and 0.2 mg/kg of chlorothalonil and lambda cyhalothrin respectively, allowed by WHO in kales (FAO/WHO 1996).

These results concur with the findings of the study carried out earlier by Shashi *et al.* (2014) which found out that, tap water, cooking directly or washing with 2% salt water did not reduce the dimethoate, methyl parathion, quinophos, endosulfan and profenophos to levels below MRL levels.

The data from Appendix II were plotted as shown in Figure 4.5 for concentration of chlorothalonil residue remaining after washing. Figure 4.6 compares the concentration of lambda cyhalothrin remaining after washing.

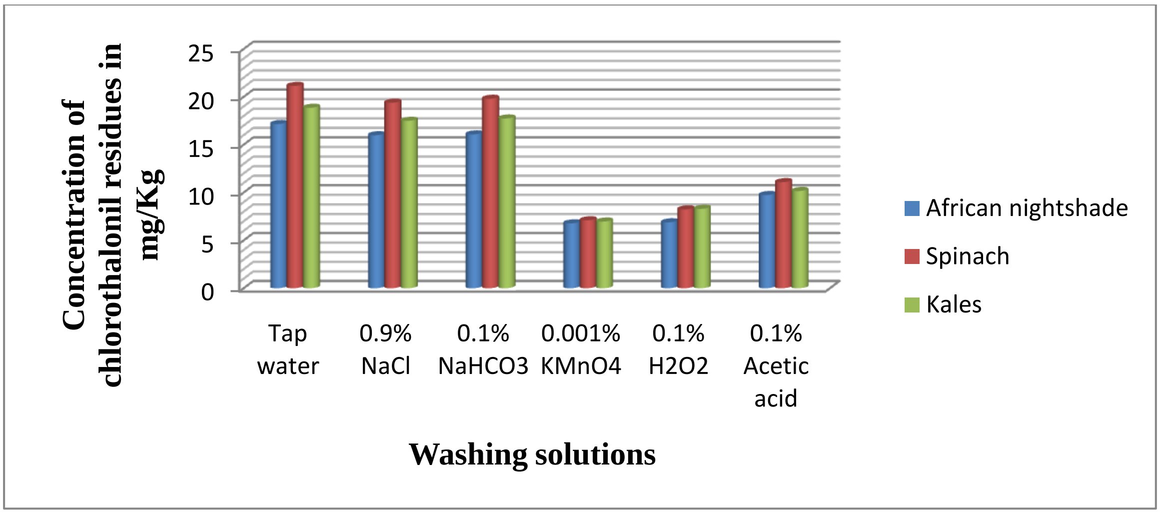

Figure 4. 5: Amount of chlorothalonil residue remaining on vegetables after washing

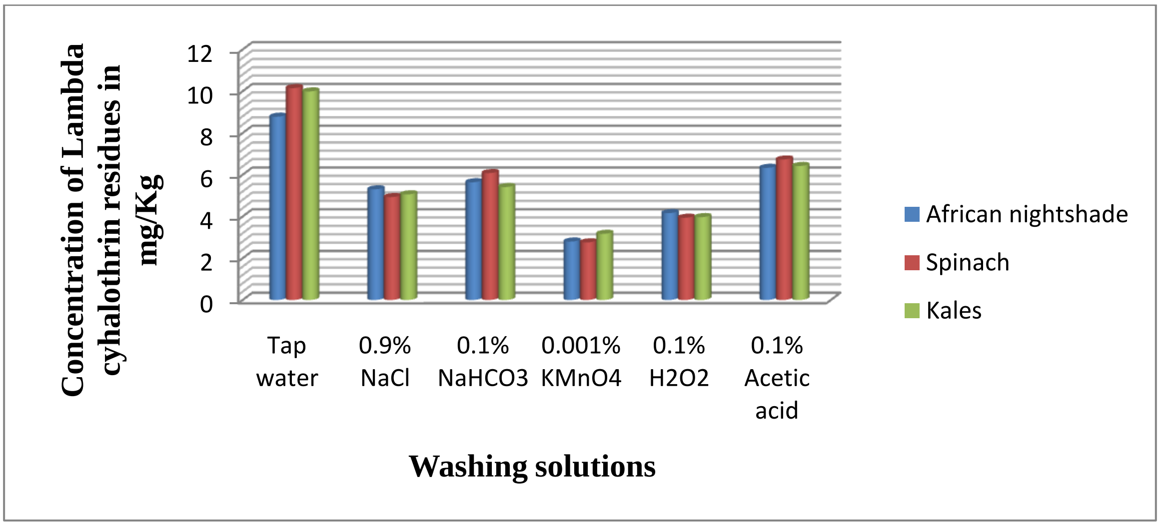

Figure 4. 6: Amount of lambda cyhalothrin residue remaining on vegetables after washing

4.6 The degradation process of pesticides in washing solutions

The study focused on the degradation of chlorothalonil and lambda cyhalothrin in 0.1% CH_3COOH, 0.9% NaCl and 0.001% $KMnO_4$ solutions. The mixture of the washing solutions and the pesticide were subjected to different durations of shaking.

4.6.1 The effect of settling time on the degradation of lambda cyhalothrin in washing solutions

The pesticide were mixed with the washing solution at a ratio of 1:9 then allowed to settle for different time intervals after which extraction of the residues from the solution was done for analysis. The concentration obtained from the analysis of the solution after the set time interval was used to determine the percentage of the pesticide residue degraded from the initial concentration which was mixed with the washing solution. The data obtained are shown in Table 4.5

Table 4.5: The percentage degradation of lambda cyhalothrin in washing solutions at varying settling times

Settling time (min)	% Degraded in 0.001% $KMnO_4$	% Degraded in 0.9% NaCl	% Degraded in 0.1% CH_3COOH
5	86.63 ±0.02	85.40 ±1.31	85.81 ±0.32
15	87.51 ±1.01	85.65 ±1.04	86.32 ±0.81
30	88.15 ±2.18	86.11 ±1.17	87.45 ±1.11
45	88.56 ±0.12	86.33 ±0.93	87.98 ±1.52
60	89.01 ±1.03	86.69 ±1.09	88.38 ±0.13

From Table 4.5, it was observed that 0.001% $KMnO_4$ degraded the highest percentage of the lambda cyhalothrin across all the time intervals ranging from 86.63 ±0.02% to 89.01 ±1.03%, this was followed by 0.1% CH_3COOH that recorded degradation of between 85.81±0.32% to 88.38 ±0.13%. The lowest degradation of lambda cyhalothrin was for 0.9% NaCl solution ranging from 85.40 ±1.31% to 86.69 ±1.09%. Similar results were obtained in a study of the degradation of pesticides residues in washing solutions by Mbugua (2015). This implies that 0.001% $KMnO_4$ is most effective washing solution for the degradation of lambda cyhalothrin pesticide residues levels (Figure 4.7).

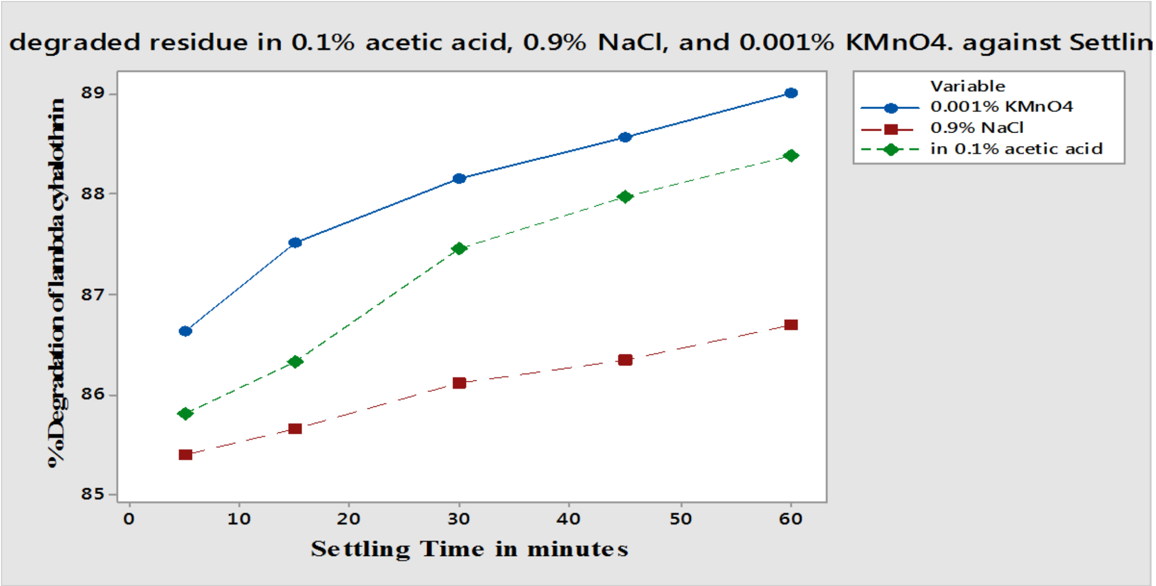

Figure 4.73: The percentage degradation of lambda cyhalothrin in washing solutions at varying settling times

The data in Table 4.5 was used to calculate the half-life ($t_{1/2}$) of lambda cyhalothrin in the washing solutions. Regression analysis was used assuming that the degradation of lambda cyhalothrin followed a first order kinetic. The regression and the $t_{1/2}$ obtained are as shown in Table 4.6.

Table 4.6: Regression and half-life of lambda cyhalothrin in 0.001% $KMnO_4$, 0.9% NaCl, and 0.1% CH_3COOH

Washing solution	R^2	Half-life (minutes)
0.001% $KMnO_4$	0.99	14.46
0.9% NaCl	0.98	288.75
0.1% CH_3COOH	0.98	59.74

The half of lambda cyhalothrin was relatively higher in 0.9% NaCl at 228.75 minutes. This may be attributed to the fact that lambda cyhalothrin is highly hydrophobic and therefore hydrolysis takes place very slowly at pH 7, in 0.001% $KMnO_4$ the half-life is short given the fact that $KMnO_4$ is a strong oxidizing agent and therefore it's able to degrade the pesticide through oxidation. Figure 4.8 shows the Regression plots of ln of concentration of lambda cyhalothrin standard residue in 0.001% $KMnO_4$, 0.9% NaCl, and 0.1% CH_3COOH.

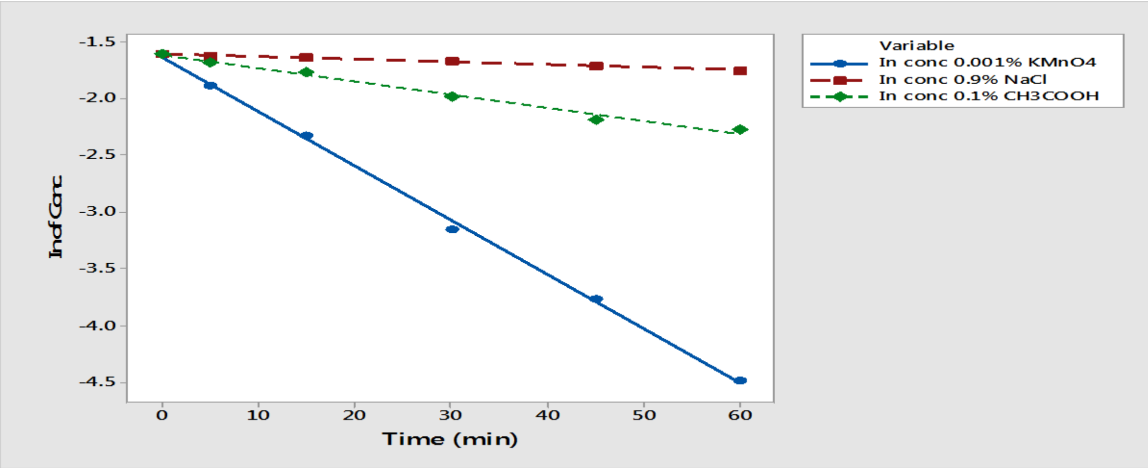

Figure 4. 8: Regression plots of ln of concentration of lambda cyhalothrin standard residue in 0.001% $KMnO_4$, 0.9% NaCl, and 0.1% CH_3COOH

4.6.2 The effect of settling time at constant shaking time on the degradation of lambda cyhalothrin in washing solutions

The results from mixing lambda cyhalothrin pesticides residues with the washing solution at a ratio of 1:9 and shaking on a mechanical shaker for 5 minutes are shown in Table 4.7 and Figure 4.9

Table 4.7: The percentage degradation of lambda cyhalothrin in washing solutions at constant shaking and varying settling times

Settling Time (Minutes)	**% Degraded in 0.001% $KMnO_4$**	**% Degraded in 0.9% NaCl**	**% Degraded in 0.1% acetic acid**
0	87.07 ± 1.05	86.41 ±0.09	85.97 ±0.61
10	88.26 ± 2.02	87.33 ±1.01	86.30 ±2.08
20	89.01 ± 0.22	88.24 ±1.10	86.50 ±0.41
30	90.15 ± 2.02	89.10 ±1.09	86.65 ±1.05
40	91.17 ± 1.32	90.76 ±2.02	86.71 ±0.11
50	92.33 ± 0.13	91.56 ±0.97	86.93 ±2.31
60	93.52 ± 2.60	92.54 ±1.31	87.76 ±0.29

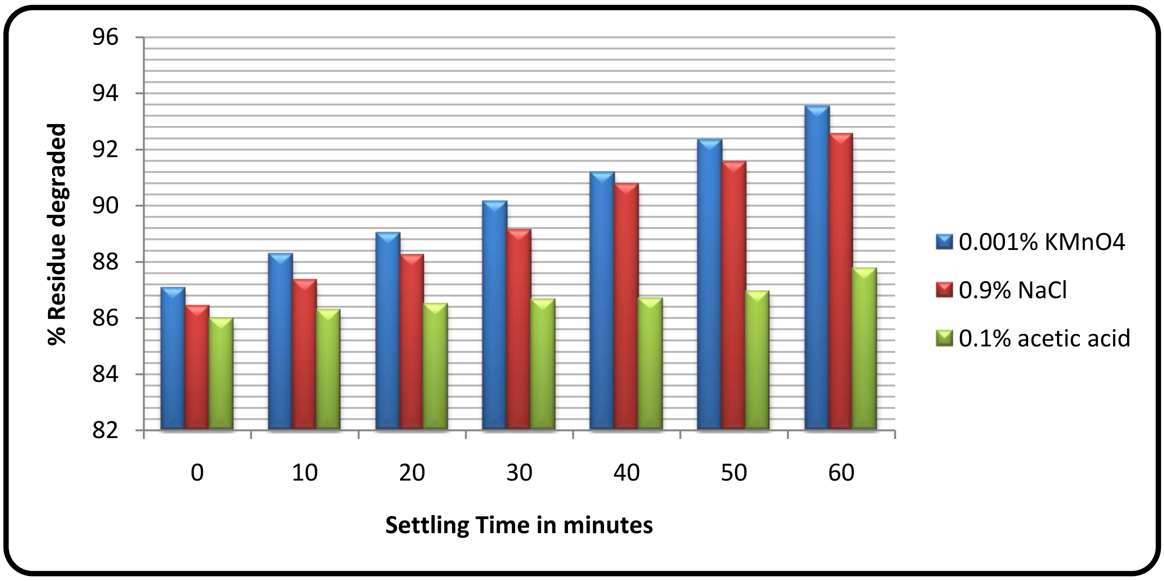

Figure 4. 9: The percentage degradation of lambda cyhalothrin in washing solutions at constant shaking and varying settling times

Lambda-cyhalothrin degradation rates by 0.001% $KMnO_4$ solution was the highest at all the time interval ranging between 87.07 ± 1.05 to 93.52 ± 2.60 %. 0.9% NaCl degraded higher pesticide residue levels than the 0.1% CH_3COOH after shaking for 5 minutes, compared to the degradation when there was no shaking of the mixture (Table 4.7). The degradation of 0.9% NaCl was between 86.41 ±0.09 and 92.54 ±1.31 % as compared to that of 0.1% CH_3COOH that ranged between 85.97 ±0.61 to 87.76 ±0.29 % (Figure 4.9)

4.6.3 The effect of shaking time at constant settling time on the degradation of lambda cyhalothrin in washing solutions

The data obtained after shaking mixture of pesticide standard solution and the washing solution on a mechanical shaker for varying time interval and settling for a constant time of 20 minutes was tabulated in Table 4.8.

Table 4.8: The percentage degradation of lambda cyhalothrin in washing solutions at varying shaking and constant settling times

Shaking Time (Min)	**Settling Time(Min)**	**% Degradation in 0.001% $KMnO_4$**	**% Degradation in 0.9% NaCl**	**% Degradation in 0.1% CH_3COOH**
0	20	88.84 ±1.12	88.22 ±0.07	87.46 ±1.02
5	20	89.69 ±1.06	89.23 ±0.75	87.99 ±0.91
10	20	89.94 ±2.01	90.44 ±1.06	88.69 ±1.41
15	20	90.72 ±1.08	91.60 ±1.13	89.33 ±1.22
20	20	91.98 ±0.92	92.57 ±0.99	89.57 ±1.11

From Table 4.8 the results shows that degradation of the lambda cyhalothrin by 0.001% $KMnO_4$ solution was higher at the beginning at 88.84 ±1.12% and 89.69 ±1.06% compared to that by 0.9% NaCl which was at 88.22±0.07% and 89.23±0.75%. However, the degradation by 0.9% NaCl surpasses that of 0.001% $KMnO_4$ as the agitation by shaking time increases. This could be due to the fact that 0.9% NaCl particles are smaller than the 0.001% $KMnO_4$ thus increase in agitations time increase the rate of degradation due to more contact time between the 0.9% NaCl and the pesticide molecules. 0.1% CH_3COOH registered the lowest degradation rate of between 87.46±1.02% and 89.57±1.11%. The values in Table 4.8 was plotted to obtain Figure 4.10

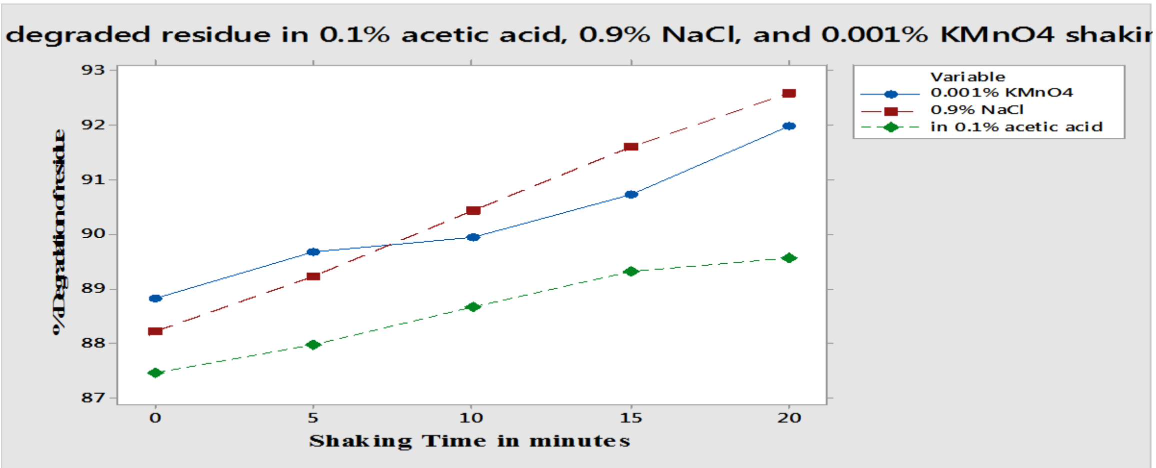

Figure 4.10: The percentage degradation of lambda cyhalothrin in washing solutions at varying shaking and constant settling times

The data in Table 4.5 (for the 30 minutes settling interval) and Table 4.8 (10 minutes shaking plus 20 minutes settling time) were statistically analyzed and the calculated values of F for one tailed test (Table 4.9) were 0.256, 1.499 and 0.122 for 0.001% $KMnO_4$, 0.9% NaCl and0.1% CH_3COOH respectively. These values were lower than the tabulated critical values of $F_{(1,4)}$ of 7.709 (P=0.05) showing that there was no significant difference between the results obtained.

Table 4.92: Critical values of F for one tailed test for degradation of lambda cyhalothrin and chlorothalonil residue levels in washing solutions

Solutions	**30 minutes settling interval**	**10 minutes shaking plus 20 minutes settling time**	**$F_{(1,4)}$ tabulated P(0.05)**	**F (calculated)**
Lambda cyhalothrin				
0.001% $KMnO_4$	4.738±0.072	4.022±0.005	7.709	0.256
0.9% NaCl	5.554±0.040	3.823±0.025	7.709	1.499
0.1% CH_3COOH	5.016±0.005	4.523±0.005	7.709	0.122
Chlorothalonil				
0.001% $KMnO_4$	6.765±0.004	5.663±0.015	7.709	0.607
0.9% NaCl	7.494±0.008	5.674±0.019	7.709	1.658
0.1% CH_3COOH	7.034±0.008	5.982±0.002	7.709	0.554

4.6.4 The effect of settling time on the degradation of chlorothalonil in washing solutions

The chlorothalonil standard was mixed with the individual washing solutions separately at a ratio of 1:9 then allowed to settle at different time intervals and pesticide residue levels extracted and solution taken for analysis. . The values obtained are shown in Table 4.10

Table 4.103: The percentage degradation of chlorothalonil in washing solution at varying settling times.

Settling Time (min)	% Degraded in 0.001% $KMnO_4$	% Degraded in 0.9% NaCl	% Degraded in 0.1% CH_3COOH
5	81.52 ±1.02	79.73 ±1.42	80.17 ±1.86
15	82.69±2.11	80.56 ±2.01	81.47 ±1.64
30	83.08 ±1.09	81.26 ±1.51	82.41 ±2.19
45	83.77±0.93	82.04 ±1.33	83.27 ±0.53
60	84.08 ±1.78	82.31 ±2.67	83.88 ±1.89

The highest chlorothalonil degradation was achieved in 0.001% $KMnO_4$ at levels ranging from 80 ±1.02 % to 84.08 ±1.78%. Degradation of the chlorothalonil in 0.1% CH_3COOH ranged between 80.17 ±1.86% and 83.88 ±1.89%, while degradation was lowest in 0.9% NaCl ranging between 79.73 ±1.42% and 82.31 ±2.67% (Table 4.10)

In comparison with the degradation of lambda cyhalothrin under the same conditions, lambda cyhalothrin degraded more in 0.001% $KMnO_4$, 0.9% NaCl and 0.1% CH_3COOH solutions (Table 4.5) than chlorothalonil residue levels (Table 4.10). The degradation rates for chlorothalonil is shown in Figure (Figure 4.11)

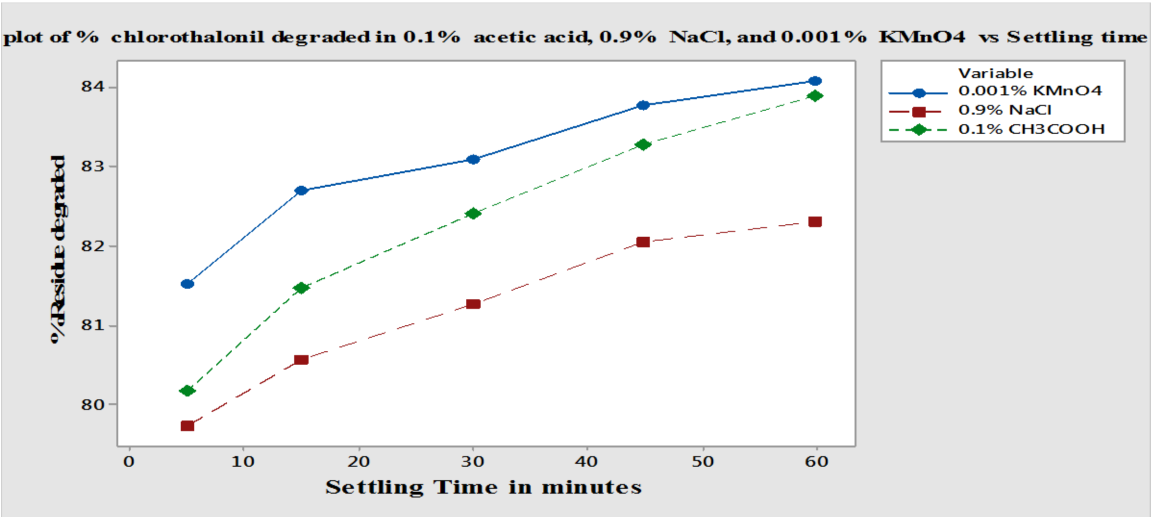

Figure 4.11: The percentage degradation of chlorothalonil in washing solution at varying settling times.

The data in Table 4.9 was used to calculate the half-life ($t_{1/2}$) of chlorothalonil in the washing solutions. Regression analysis was used assuming that the degradation of chlorothalonil followed a first order kinetic. The regression and the $t_{1/2}$ obtained are as shown in table 4.11. Figure 4.12 shows the Regression plots of ln of concentration of chlorothalonil standard residue in 0.001% $KMnO_4$, 0.9% NaCl, and 0.1% CH_3COOH.

Table 4.11: Regression and half-life of Lambda cyhalothrin in 0.001% $KMnO_4$, 0.9% NaCl, and 0.1% CH_3COOH

Washing solution	R^2	Half-life (minutes)
0.001% $KMnO_4$	0.980	20.50
0.9% NaCl	0.974	100.43
0.1% CH_3COOH	0.970	36.47

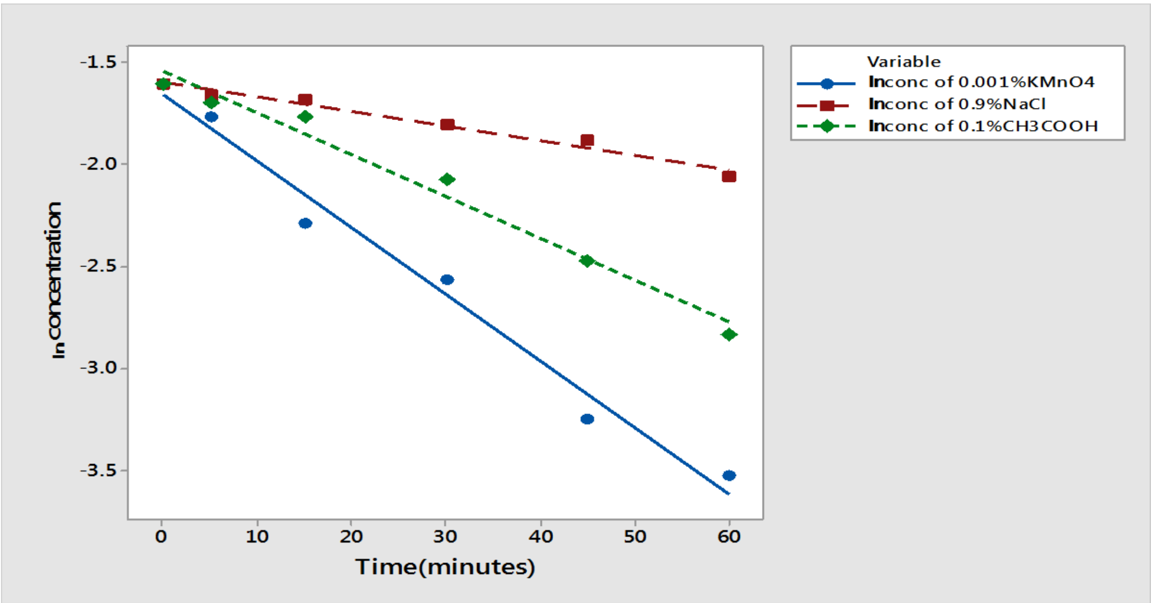

Figure 4.12: Regression plots of ln of concentration of Chlorothalonil standard residue in 0.001% $KMnO_4$, 0.9% NaCl, and 0.1% CH_3COOH

4.6.5 The degradation of chlorothalonil in washing solution at constant shaking and varying settling times

The study of degradation of chlorothalonil standard pesticide solution in various washing solutions under conditions of 5 minutes shaking on a mechanical shaker and different settling time intervals was carried out. The data obtained was tabulated in Table 4.12.

Table 4.12: The percentage degradation of chlorothalonil in washing solution at constant shaking and varying settling times.

Settling Time	**% Degraded in 0.001% $KMnO_4$**	**% Degraded in 0.9% NaCl**	**% Degraded in 0.1% acetic acid**
0	87.33 ±1.04	85.80 ±1.06	81.62 ±1.49
10	88.25 ±0.93	87.22 ±1.22	82.58 ±1.29
20	88.78 ±1.02	87.69 ±1.03	83.24 ±0.89
30	89.13 ±2.01	88.18 ±0.81	83.95 ±1.53
40	89.71 ±1.92	88.68 ±1.13	84.66 ±1.61
50	90.14 ±2.15	89.07 ±0.97	84.97 ±1.17
60	90.72 ±1.24	89.60 ±1.19	85.47 ±1.78

After shaking the solutions for constant time of 5 minutes the degradation of chlorothalonil was highest in 0.001% $KMnO_4$ solution in the range of 87.33 ±1.04% and 90.72 ±1.24%. Degradation in 0.1% CH_3COOH registered the lowest value of between 81.62 ±1.49% to 85.47 ±1.78%. Degradation of the chlorothalonil in 0.9% NaCl ranged between 85.80 ±1.06% to 89.60 ±1.19%, surpassing degradation in 0.1% CH_3COOH as compared to when there was no agitation by shaking the mixture. It can also be noted that degradation of the pesticide increases with shaking of the solution (Figure 4.13).

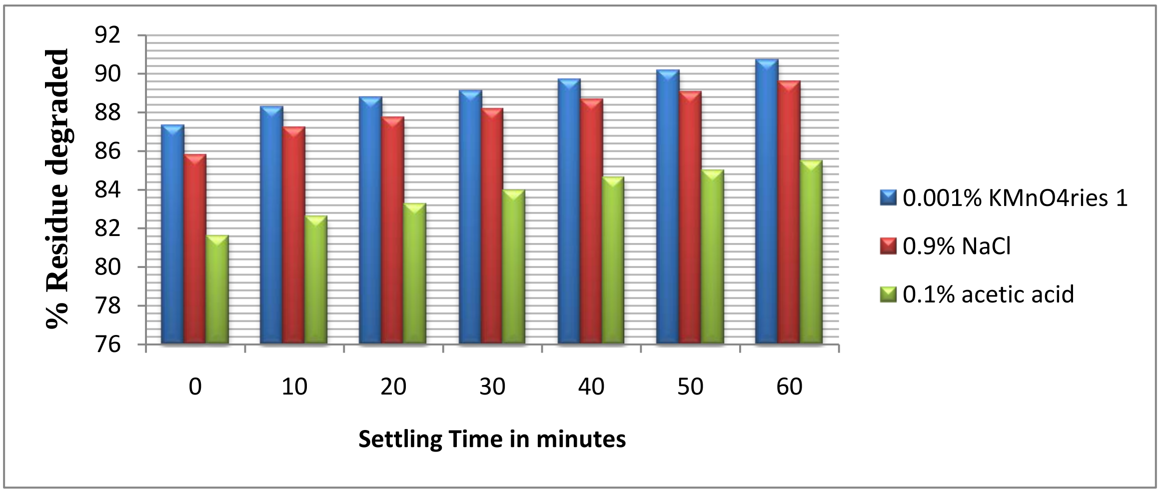

Figure 4.13: The percentage degradation of chlorothalonil in washing solution at constant shaking and varying settling times.

4.6.6 The degradation of chlorothalonil in washing solutions at varying shaking time and constant settling times

The chlorothalonil pesticide standard was mixed with the washing solutions separately at a ratio of 1:9 then shaken on a mechanical shaker for varying time intervals, the mixture were then removed from the shaker and allowed to settle for 20 minutes after which extraction of the residues from the solution was done for analysis. The data obtained was tabulated in Table 4.13 and plotted to obtain Figure 4.14

Table 4.13: The percentage degradation of chlorothalonil in washing solution at varying shaking times.

Shaking Time (Min)	**Settling Time(Min)**	**% Degraded in 0.001% $KMnO_4$**	**% Degraded in 0.9% NaCl**	**% Degraded in 0.1% CH_3COOH**
0	20	84.96 ±1.03	83.61 ±1.14	83.35 ±1.93
5	20	85.55 ±2.25	85.36 ±2.49	84.07 ±1.68
10	20	85.84 ±0.97	85.81 ±1.04	85.04 ±2.51
15	20	86.04 ±1.81	86.35 ±1.84	85.47 ±1.09
20	20	86.55 ±1.12	86.97±1.36	85.93 ±1.67

From table 4.13 the degradation of chlorothalonil in 0.1% CH_3COOH registered the lowest degradation under this condition ranging from 83.35 ±1.93% to 85.93 ± 1.67%. However, these degradations are higher than when there was no shaking of the mixture or when the shaking is done for 5 minutes only as noted for lambda cyhalothrin standard. The degradation of the chlorothalonil by 0.001% $KMnO_4$ was higher at the beginning at 84.96 ±1.03% and 85.55 ±1.12% than that of 0.9% NaCl which was at 83.61 ±1.14% and 85.36 ±2.49%, however it is noted that as the shaking duration increases the degradation of the chlorothalonil by 0.9% NaCl surpasses that of 0.001% $KMnO_4$ and therefore registered the highest reduction of 86.97 ±1.36% as compared to that registered by 0.001% $KMnO_4$ of 86.55 ±1.12%.

The data in Table 4.10 (for settling time of 30 minutes) and Table 4.13 (for 10 minutes shaking time plus 20 minutes settling time) were statically analyzed and the one tailed test values of F obtained (Table 4.9) were 0.607, 1.658 and 0.554 for 0.001% $KMnO_4$, 0.9% NaCl and 0.1% CH_3COOH respectively. The calculated values were smaller than the tabulated critical values of $F_{(1,4)}$ of 7.709 (P=0.05), showing no significant difference between the means in Tables 4.10 and 4.13.

The graphical representation of the data tabulated in Table 4.13 was obtained by plotting the percentage of the residue degraded against time as shown in Figure 4.14.

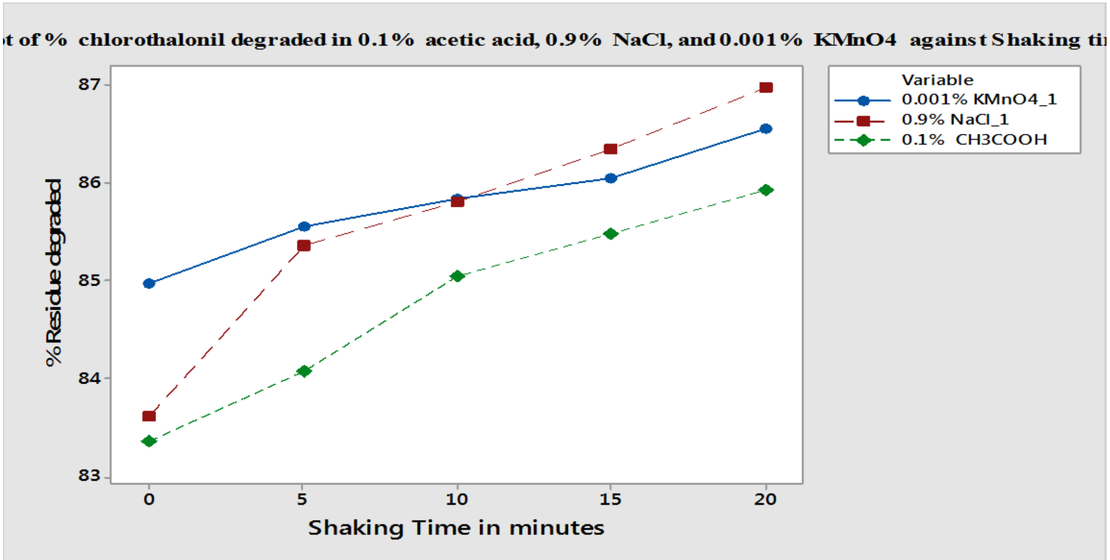

Figure 4.14: The percentage degradation of chlorothalonil in washing solutions at varying shaking times.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The study found that the African nightshade, spinach and Kales vegetables sold at City Park Market in Nairobi County were contaminated with chlorothalonil and lambda cyhalothrin pesticide residues. The residue levels of lambda cyhalothrin were 0.034 ±0.003 mg/Kg and 0.03 ±0.002 mg/Kg in Spinach and Kales, respectively. This was below MRL levels (0.200 mg/Kg and 0.100 mg/Kg for Kales and Spinach respectively) while those of chlorothalonil were 0.14 ±0.013 mg/Kg in spinach, 0.100 ±0.007 mg/Kg in Kales and 0.002 ±0.001 mg/Kg in African nightshade. All these were above the MRL levels (0.040 mg/Kg). Chlorothalonil was more adsorbed on the vegetable leaves as compared to the lambda cyhalothrin. Spinach leaves adsorbed the highest levels of the two pesticides followed by the Kales, while African nightshade had the least absorbance of the pesticides.

0.001% $KMnO_4$ solution was the most effective in removal of the pesticide residue from the vegetable with an average of 83.54 ±2.97% lambda cyhalothrin and 67.65 ±3.20% chlorothalonil removal from the vegetables. The tap water was the least effective washing method with an average of 45.84 ±2.35% lambda cyhalothrin and 10.85 ±1.92% chlorothalonil removal from the vegetables. The amount of the pesticide residue left on the vegetables after washing was a relatively higher than the MRL levels.

The degradation of the lambda cyhalothrin residues was highest in 0.001% $KMnO_4$ solution ranging from 86.63 ±0.02% to 89.01 ±1.03% while 0.9% NaCl registered the lowest degradation ranging from 85.40 ±1.31% to 86.69 ±1.09%. The degradation of the chlorothalonil residues was highest in 0.001% $KMnO_4$ ranging from 81.52 ±1.02% to 84.08 ±1.78% while 0.9% NaCl registered the lowest degradation ranging from 79.73 ±1.42% to 82.31 ±2.67%.

Agitation of chlorothalonil and lambda cyhalothrin standard residues and washing solution mixture by shaking increased the percentage degradation of the pesticide. 0.9% NaCl registered the highest degradation for increased shaking duration registering between 88.22

±0.07% and 92.57 ±0.99% degradation of lambda cyhalothrin and 83.61 ±1.14% to 86.97 ±1.36% degradation of chlorothalonil.

5.2 Policy recommendations from this work

From the data obtained and the discussions from this study the following recommendations are made.

i. The public should be made aware of the pesticide residues in vegetables bought at the City Park market and be sensitized of the dangers of the pesticides on their health and environment.
ii. The KEBS should come up with a policy on the analyzing for pesticide residues on vegetables sold at the markets in the country so as to ensure only vegetables within the MRL levels are in the markets.
iii. Vegetable consumers to be advised on thorough washing of the vegetables with household washing solutions such as NaCl and low concentration CH_3COOH.
iv. The government should ensure that vegetables sold at City markets are fit for consumption by its population.

5.3 Recommendations for further research work

Further research study is recommended so as to:

i. The pesticide residues levels should also be analyzed from vegetable samples obtained from markets in other parts of the country.
ii. The metabolites of the degradation products after the degradation of the pesticides in washing solution should be determined.
iii. The degradation of the pesticides when shaking is coupled with other conditions such as variation of temperature and pH should be determined.
iv. The studies of determining the degradation mechanisms of the pesticides residues in different washing solutions should also be carried out.

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APPENDIX I:

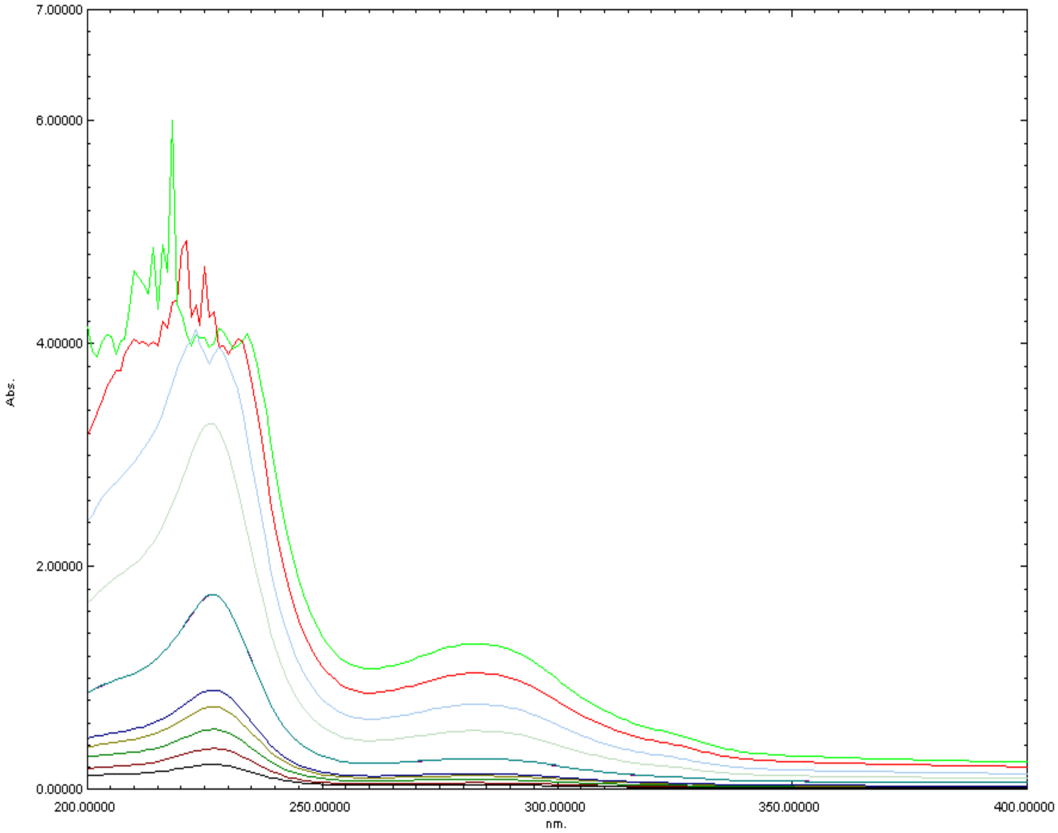

Figure 4: The UV/Vis scans for the concentration of lambda cyhalothrin

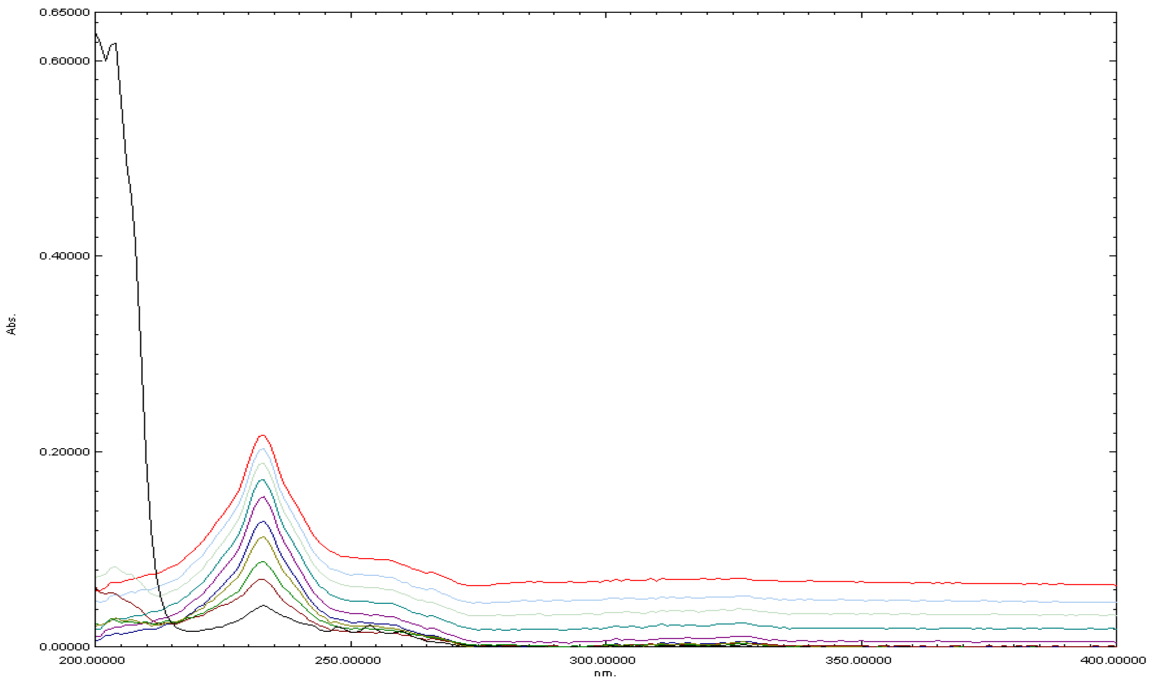

Figure 5: The UV/Vis scans for the concentration of for chlorothalonil

APPENDIX II: Percentage of pesticide residue removal from vegetables by washing solutions

African nightshade						
Chlorothalonil				**Lambda cyhalothrin**		
Solutions	Initial level (mg/kg)	Amount left after washing (mg/kg)	% Amount removed	Initial level (mg/kg)	Amount left after washing (mg/kg)	% Amount removed
Tap water	19.12 ±1.51	17.16±0.38	10.23 ±2.00	16.50±3.02	8.78±0.33	46.76 ±2.67
0.9% NaCl	19.12 ±1.51	15.99±0.19	16.34 ±1.30	16.50 ±3.02	5.30±0.49	67.87 ±3.09
0.1% $NaHCO_3$	19.12 ±1.51	16.08±1.57	15.87 ±3.05	16.50 ±3.02	5.64±0.16	65.78 ±1.43
0.001% $KMnO_4$	19.12 ±1.51	6.78±0.75	65.67 ±3.73	16.50 ±3.02	2.80±0.16	82.97 ±1.63
0.1% H_2O_2	19.12 ±1.51	6.89±2.54	63.93 ±3.04	16.50 ±3.02	4.16±0.33	74.78 ±2.78
0.1% Acetic acid	19.12 ±1.51	9.74±2.01	49.03 ±1.84	16.50 ±3.02	6.33±0.49	61.67 ±3.23
Spinach						
Tap water	23.87 ±2.67	21.14±0.47	11.43 ±0.21	19.70 ±0.54	10.15±0.39	48.43 ±1.91
0.9% NaCl	23.87 ±2.67	19.39±0.23	18.76 ±1.56	19.70 ±0.54	4.93±0.39	74.95 ±2.72
0.1% $NaHCO_3$	23.87 ±2.67	19.80±0.41	17.01 ±2.72	19.70 ±0.54	6.08±0.59	69.09 ±3.07
0.001% $KMnO_4$	23.87 ±2.67	7.10±0.71	70.23 ±3.82	19.70 ±0.54	2.76±0.78	85.98 ±4.19
0.1% H_2O_2	23.87 ±2.67	8.24±0.21	65.46 ±1.75	19.70 ±0.54	3.94±0.59	79.97 ±3.28
0.1% Acetic acid	23.87 ±2.67	11.09±0.37	53.54 ±2.06	19.70 ±0.54	6.73±0.59	65.87 ±3.08

Kales						
Chlorothalonil				**Lambda cyhalothrin**		
Solutions	Initial level (mg/kg)	Amount left after washing (mg/kg)	% Amount removed	Initial level (mg/kg)	Amount left after washing (mg/kg)	% Amount removed
Tap water	21.17 ±1.91	18.86±0.21	10.90 ±1.09	17.34 ±2.37	9.99±0.34	42.34 ±2.47
0.9% NaCl	21.17 ±1.91	17.50±0.42	17.34 ±2.01	17.34 ±2.37	5.06±0.52	70.78 ±3.19
0.1% $NaHCO_3$	21.17 ±1.91	17.74±1.63	16.17 ±3.50	17.34 ±2.37	5.41±0.17	68.76 ±1.79
0.001% $KMnO_4$	21.17 ±1.91	6.97±0.76	67.06 ±2.04	17.34 ±2.37	3.17±0.52	81.68 ±3.03
0.1% H_2O_2	21.17 ±1.91	8.30±0.85	60.76 ±3.01	17.34 ±2.37	3.97±0.17	77.07 ±1.86
0.1% Acetic acid	21.17 ±1.91	10.16±0.71	51.98 ±1.78	17.34 ±2.37	6.42±0.17	62.93 ±1.08