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Fate and Mobility of *Imidacloprid* and *Abamectin* Residues in Green House Soil

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Dedication

To the spirit of my father, who had sacrificed intently for the sake of our Education before he passed away. To my beloved mother, wife, brothers, sisters and to my lovely children; Zuhra and Zaid with love.

To everyone who cares about the environment and works to save it Respect.

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Osama

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Fate and Mobility of *Imidacloprid* and *Abamectin* Residues in Green House Soil

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تم الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أي درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

<u>Declaration</u>

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name: **اسم الطالب:**

Signature   **التوقيع:**

Date: **التاريخ:**

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List of Abbreviation

symbol	Abbreviation
A	Intra-particle diffusion constant gives an idea about the thickness of the boundary layer.
Ach	Acetyl choline.
b	Langmuir constant related to the rate of adsorption.
k1	Equilibrium rate constant of pseudo-first-order kinetic model.
k2	Equilibrium rate constant of pseudo-second-order kinetic model.
K_F	Freundlich constant represents the quantity of adsorbate onto soil per a unit equilibrium concentration.
n	Freundlich constant.
qe	Amount of adsorbate per unit mass of adsorbent at equilibrium(min).
qt	Amount of adsorbate per unit mass of adsorbent at time t (min).
R2	Correlation coefficient.
GDP	Gross Domestic Product.
OP	Organophosphate.
IGR	Insect Growth Regulator.
ARIJ	Applied Research Institute-Jerusalem.
PNA	Palestinian National Authority.
DDE	Dynamic Data Exchange.
nAChR	Nicotinic acetylcholine receptor.
DPR	Department of pesticide Regulator.
DT50	Dissipation Time.
LD50	Lethal Dose.
LC50	Lethal Concentration.
GABA	Gamma-amino butyric acid.
HPLC	High Performance Liquid Chromatography.
Mcf	Moisture correction factor.
WHO	World Health Organization.
$\Delta H°$	Standard enthalpy.
$\Delta S°$	Standard entropy.
$\Delta G°$	Standard free energy.

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Abstract

Recently, one of the most indispensable methods in the usage of pesticides in agriculture and crops which make great improvement toward this crops. On the other hand there are demerits of using such pesticides toward the human health.

In this study two pesticides were selected, imidacloprid (Konfidor [®]) and abamectin (Vertimec [®]) as examples of pesticides that are released into the environment, both are marketed in the Palestinian market, and the widely used in Palestine based on the results of the survey that was conducted.

In this research we have investigated the adsorption behavior of the two pesticides on soil, the effect of temperature, pH, adsorbent dosage, contact time and concentration on the adsorption process, all were studied using UV-Vis spectrophotometry.

Results indicate the highest percentage of imidacloprid and abamectin removal was 13.4 % and 7.5 % respectively when adsorbent dosage 3 g. percentage removal of imidacloprid and abamectin increases when the concentration decreases, the maximum percentage removal reached 17 % for imidacloprid and 19 % for abamectin when their concentrations was 10

mg/L and 1 g soil. At low pH "1.5" the percentage of imidacloprid removal increases reached to 12.3 %, but the decrease of imidacloprid removal at high pH "12" is highly extreme reached to 7.3 % . At high pH "12" the percentage of abamectin removal increases reached to 15.4 %, but the lowest percentage of abamectin removal at pH 7 reached to 9.1 %. The effect of temperature on adsorption by soil has also been investigated in the range of 15–47°C. The results indicate that imidacloprid and abamectin soil adsorption in this study was increased with increasing temperature. The results showed that the equilibrium time for imidacloprid and abamectin adsorption is 150 min, but most of the adsorption attained within the first 15 min.

This study was aimed to assess the adsorption, leaching potential, fate and mobility of imidacloprid and abamectin in soil. To understand mechanism of adsorption and factors affecting , the experiments were carried out under laboratory conditions. Adsorption study was divided into kinetic and equilibrium sections. The evaluation of kinetic data was done through pseudo first and second order models and intra-particle diffusion model. It was found that kinetic adsorption of imidacloprid and abamectin on soil followed pseudo second order. Langmuir and Freundlich isotherms were used to explain equilibrium adsorption, from these isotherms it was evaluated that Freundlich isotherm was obeyed well.

Chapter One

1.1 General Introduction

Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, **(Peter, *et al,*2010).**

Pesticides are a special kind of products for crop protection. Crop protection products in general protect plants from damaging influences such as weeds, diseases or insects. A pesticide in generally a chemical or biological agent (such as a virus, bacterium, antimicrobial or disinfectant) that through its effect deters, incapacitates, kills or otherwise discourages pests. Target pests can include insects, plants pathogens, weeds, molluscs, birds, mammals, fish, nematodes(roundworms), and microbes that destroy property, cause nuisance, spread disease or are vectors for disease. Although there are human benefits for the use of pesticides, some also have drawbacks, such as potential toxicity to humans and other animals. Pesticides are categorized into four main substituent chemicals: herbicides, fungicides, insecticides and bactericides,**(Gilden, *et al.,* 2010).**

Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops,**(Nic. *et al,* 2006).** Many of these chemical residues, especially derivatives of chlorinated pesticides, exhibit bioaccumulation which could build up to harmful levels in the body as well as in the environment,**(Crinnion, 2009).**

Health impact to pesticide exposures can produce two distinct types of adverse health effects – acute (short-term) effects and chronic (long-term) effects. The severity of adverse health effects are determined by following

factors: the dose, the route of exposure, an individuals genetic vulnerability, age at the time of exposure and general health conditions, the length of exposure, environmental factors and intakes with other chemicals through other factors,**(Kishor, 2008).**

Environmental exposure of humans to agrichemicals is common and results in both acute and chronic health effects, including acute and chronic neurotoxicity (insecticides, fungicides, fumigants), lung damage, chemical burns, and infant methemoglobinemia (nitrate in groundwater). A variety of cancers also have been linked to exposure to various pesticides, particularly hematopoietic cancers.

 Immunologic abnormalities and adverse reproductive and developmental effects due to pesticides also have been reported. The health effects associated with pesticides do not appear to be restricted to only a few chemical classes,**(Dennis, 1993).**

Recent studies show that young children can be exposed to pesticides during normal oral exploration of their environment and their level of dermal contact with floors and other surfaces. Children living in agricultural areas may be exposed to higher pesticide levels than other children because of pesticides tracked into their homes by household members, by pesticide drift, by breast milk from their farm worker mother, or by playing in nearby fields, **(Eskenazi, *et al*., 1999)**.

1.2 Objectives:

The study aims to achieve a set of goals and most important of which are the following:

1. To raise awareness of the issue of pesticide residues for those involved in the production, supply and marketing of the fresh produce.

2. To study the fate and mobility of those pesticides in soil, and to understand the kinetics behind them and how they can reach groundwater.

1.3 Justification:

Our overall goal is to clarify the significance of pesticides use practices. The Palestinian farmers use major amounts of pesticides and have an enviable record of safety. The target audiences of this research are consumers, activists, regulators and risk assessors. All concerned including the agrochemical industry and growers will benefit from principles related to enhancing the perception of pesticide use in the greenhouses and open fields.

The fundamental reality is that people and pests are both consumers, but only people pay for the nutritional benefits and pleasure of eating fruits and vegetables. For pests, it is a matter of survival. Lygus bugs, botrytis, powdery mildew, cutworms and other, pests are expensive –free-loaders to have around. In response, pesticide use cutworm's potential human exposure at some level. The industry has an enviable safety record of safe pesticides use. Farmers set high standards for persons who pick or do other

field work. Following a pesticide application, picking time is set by expectation (the days between spraying and when residues are below – tolerance). It is maximum amount of term implies safety, in fact; the term *tolerance* refers to maximum amount of residue expected following use of a product following good agricultural practices. Amounts that are far greater than tolerances also safe relative to Low observed overestimated human pesticide exposures from eating produce reduces consumer confidence in the food supply, including the wholesomeness of fruits and vegetables. The pesticide residues are well below tolerance at all times. The non-toxic breakdown products that are formed last much longed than the pesticide itself.

Chapter Two

2. Background

2.1 Types of pesticides

2.1.1 Types of pesticides according the target organism

There are different types of pesticides and a classification is offered according the target organism. A biocide is a chemical that kills a wide range of living organisms. More specific substances are named after their target organism. Herbicides are designed to kill plants, fungicides kill fungi, and insecticides kill insects. Specific pesticides include: acaricides, nematicides, and rodenticides, (**Cunningham,** *et al.***, 2003).**

2.1.1.1 Herbicides

Herbicides, also commonly known as weedkillers, are pesticides used to kill unwanted plants. Selective herbicides kill specific targets, while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often synthetic "imitations" of plant hormones. Herbicides used to clear waste ground, industrial sites, railways and railway embankments are not selective and kill all plants material with which they come into contact. Smaller quantities are used in forestry, pasture systems, and management of areas set aside as wildlife habitat,**(Freemark and Boutin, 1995).**

2.1.1.2 Fungicides

Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores. Fungus's are a tiny plantlike organism that gets its nourishment from other living or nonliving things. Fungi can cause

serious damage in agriculture, resulting in critical losses of yield, quality and profit . fungicides are used both in agriculture and to fight fungal infections in animals and humans. Chemicals used to control oomycetes, which are not fungi, are referred to as fungicides because they use the same mechanisms as fungi to infect plants,**(McGrath, 2009).** Fungicides can either be contact, translaminar or systemic. Contact fungicides are not taken up into the plant tissue, and only protect the plant where the spray is deposited; translaminar fungicides redistribute the fungicide from the upper, sprayed leaf surface to the lower, unsprayed surface; systemic fungicides are taken up and redistributed through the xylem vessels to the upper parts of the plant. New leaf growth is protected for a short period,**(Mercer and Ruddock, 2003).**

2.1.1.3 Insecticides

An insecticide is a pesticide used against insects. They include ovicides and larvicides used against the eggs and larvae of insects respectively. Insecticides are used in agriculture, medicine, industry and the household. The use of insecticides is believed to be one of the major factors behind the increase in agricultural productivity in the 20th century,**(Cameron, *et al.*, 2009)** Nearly all insecticides have the potential to significantly alter ecosystems; many are toxic to humans; and others are concentrated in the food chain,**(Narahashi, 2001).**

2.1.1.4 Acaricides

Acaricides are pesticides that kill members of the arachnid order Acari group , which includes ticks and mites. Acaricides are used both in

medicine and agriculture, although the desired selective toxicity differs between the tow fields,**(Boncristiani, *et al*., 2012).**

2.1.1.5 Nematicides

A nematicide is a type of chemical pesticide used to kill plant-parasitic nematodes. Nematicides have tended to be broad-spectrum toxicants possessing high volatility or other properties promoting migration through the soil,**(Karpouzas, *et al*., 2007).**

2.1.1.6 Rodenticides

Rodenticides are a category of pest control chemicals intended to kill rodents. Single feed baits are chemicals sufficiently dangerous that the first dose is sufficient to kill,**(Tosh, et al., 2011).** Rodents are difficult to kill with poisons because their feeding habits reflect their place as scavengers. They will eat a small bit of something and wait, and if they do not get sick, they continue. An effective rodenticide must be tasteless and odorless in lethal concentrations, and have a delayed effect,**(Andre and Guillaume, 2004).**

2.2 Situation of agriculture in Palestine

Agriculture remains a dominant sector of the Palestinian economy. It represents a major component of the economy's GDP, and employs a large fraction of the population. Furthermore, the agricultural sector is a major earner of foreign exchange and supplies the basic needs of the majority of the local population. In times of difficulty, the agricultural sector has acted as a buffer that absorbs large scores of unemployed people who lost their jobs in Israel or other local sectors of the economy.

Palestinian agriculture is constrained by available land and water, as well as access to markets. These constraints have been the object of political conflict, as Israeli authorities have limited available land, water and markets. It is widely recognized that resolution of these conflicts is essential to the establishment of peace in the region. Since Palestinian agriculture is a major potential user of land and water, it is important to establish its needs for these resources. Typically, models for the allocation of water in the region have used a simple derived demand function for water, in which the elasticity of demand is the key parameter.

The agricultural sector was hit hard after Israel occupied the West Bank and Gaza Strip. Thereafter the sector's contribution to Gross Domestic Product (GDP) in the Palestinian Occupied Territories declined. Between 1968/1970 and 1983/1985 the percentage of agricultural contribution to the overall GDP in the West Bank fell from 37.4-53.5% to 18.5-25.4%,**(ARIJ,2000).**

Israel has restricted Palestinian water usage and exploited Palestinian water resources after occupation. Presently, more than 85% of the Palestinian water from the West Bank aquifers is taken by Israel, accounting for 25.3% of Israel's water needs. Palestinians are also denied their right to utilize water resources from the Jordan and Yarmouk Rivers, to which both Israel and Palestine are riparians. West Bank farmers historically used the waters of the Jordan River to irrigate their fields, but this source has become quite polluted as Israel is diverting saline water flows from around Lake Tiberias into the lower Jordan. Moreover, Israeli diversions from Lake Tiberias into

the National Water Carrier have reduced the flow considerably, leaving Palestinians downstream with little water of low quality,**(Butterfield, 2000).**

Agriculture is a foundation of the Palestinian nation and is an integral component of Palestinian culture economic and social life. Before 8000 BC, since the time of the Alntovip civilization, Palestinians were pioneers and innovators in agriculture and agricultural production knowledge, which inspired those both in and outside the region. Today, agriculture remains of great significance to Palestinians, symbolizing the crux of Palestinian national identity, of which affiliation with the land is at core. Agriculture symbolizes resilience against land confiscations and Israeli settlement activity and provides protection against both income and food insecurity during times of crisis. The Agricultural Sector is a pillar of the Palestinian national economy, a principal driver of economic growth, yielding large contributions to GDP, including dividends from commodity exports, and employing thousands of Palestinian men, women and youth. In addition, agriculture constitutes a major source of informal income for thousands of Palestinian families that is usually not considered in national statistics, protects Palestinian water rights and entitlements, and contributes to environmental protection sustainability. The total added value of the Sector has increased from USD 500 million in 2007 to USD 800 million in 2008,**(ARIJ, 1995).**

2.3 Situation of pesticides in Palestine

The problem of agricultural pesticide utilization in the Arab countries is not only an issue of uncontrolled use, but it is also a problem pertaining to the handling, misuse and disposal of unwanted pesticides. This is exacerbated by undeveloped national laws and regulations in regards to potential fate and residuals impacts of pesticides on groundwater, food safety and public health. Extensive use of pesticides with residual contents exceeding the maximum residue limits on produce, urged many European countries to ban certain agricultural exports from several Arab countries,**(Bashour, 2008).**

Palestine, like other Arab countries, the uncontrolled use, handling and misuse of pesticides caused an increase in types and numbers of pesticides, exacerbated by shortage of reliable data and knowledge gab on quantities utilized alerted the scientific community and the public about the health hazards of pesticides and their indiscriminate use,**(Samhan, 2008).**

Most of agricultural land in the Palestinian National Authority (PNA) is used to grow vegetables, orchards and dry land crops for food production. The latter consumes huge quantities of water and pesticides, with more people working intensively. In the PNA, people work on small plots in family owned small greenhouses, and large orchards, where agriculture employs about 30% of the 5 million PNA population,**(ARIJ, 1995).**

2.4 Fate and Mobility of Pesticides in the Environment

Pesticide persistence often is expressed in terms of half-life. This is the length of time required for one-half of the original quantity to break down

pesticides can be divided into three categories based on half-lives: non persistent pesticides with a typical soil half-life of less than 30 days, moderately persistent pesticides with a typical soil half-life of 30 to100 days, or persistent pesticides with a typical soil half-life of more than 100 days.

Pesticide mobility may result in redistribution within the application site or movement of some amount of pesticide off site. After application, a pesticide may: attach (sorb) to soil particles, vegetation, or other surfaces and remain near the site of deposition, attach (sorb) to soil particles and move with eroded soil in runoff or wind, dissolve in water and be taken up by plants move in runoff , or leach, volatilize or erode from foliage or soil with wind and become airborne, Mobility is affected by the pesticide's sorption water solubility and vapor pressure. Mobility also, is influenced by environmental and site characteristics including weather, topography, canopy, and ground cover; and soil organic matter, texture, and structure,**(Bloomfield, et al., 2006).**

When pesticides are applied to places such as homes, offices, lawns, gardens, fields, and water sources they become mobile in the environment (**McDonald, et al., 1999).**

The fate of pesticides in the environment is analyzed considering the processes that determine their persistence and mobility, grouped into transport, transfer and transformation processes. Few pesticide characteristics such as persistence, mobility and biodegradability are emphasized. The fate of a pesticide and the potential for its persistence and

mobility from the site of application are considered to be affected by the chemical and physical properties of the pesticide, site characteristics such as soil and groundwater individuality, climate and local weather conditions, biological population, and the handling practices of the pesticide user,(**Gavrilescu, 2005**).

Pesticides may become airborne, get into soil, enter bodies of water, or be taken up by plants and animals. The environmental fate of pesticides depends on the physical and chemical properties of the pesticide as well as the environmental conditions. The physical and chemical properties of the pesticide determine how likely it is to travel through soil (soil mobility), how well it dissolves in water (water solubility), and how likely it becomes airborne (volatility),(**Solomon, 2001**).
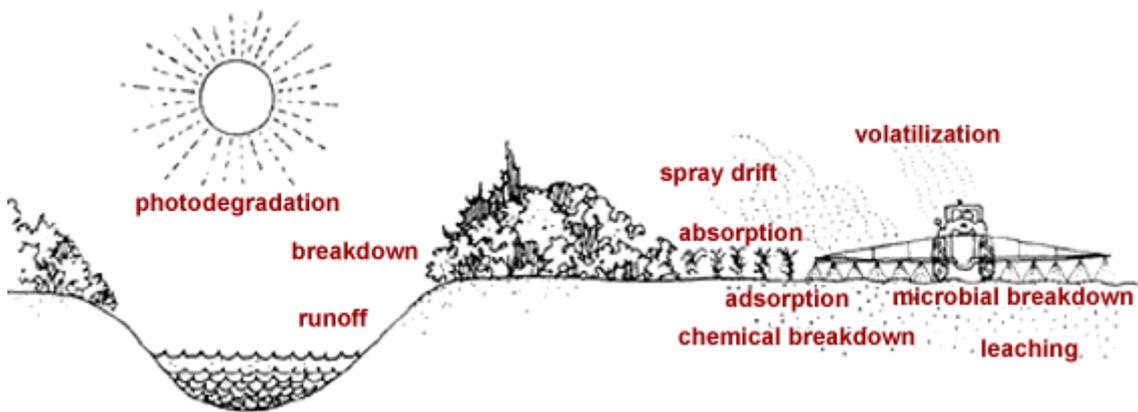
Figure 2.1 Fate of Pesticides in Environment

2.4.1 Fate and Mobility of Pesticides in Air

Pesticides can contribute to air pollution. Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. Pesticides that are applied to crops

can volatilize and may be blown by winds into nearby areas, potentially posing a threat to wildlife,**(Harrison, 2008).** Weather conditions at the time of application as well as temperature and relative humidity change the spread of the pesticide in the air. As wind velocity increases so does the spray drift and exposure. Low relative humidity and high temperature result in more spray evaporating. The amount of inhalable pesticides in the outdoor environment is therefore often dependent on the season,**(Gouin, *et al.,* 2008).**

Pesticides, regardless of the medium that they are applied in, all have the potential to be transported by air. Airborne pesticides can move very long distances and can occur in several ways. They can be carried in the wind during application. They can be carried on small particulates such as soil or on larger objects like leaves that are caught up by wind, and they can volatilize off of any surface that they are applied to. Deposition is what occurs when the wind carrying a pesticide slows down enough that its velocity can no longer hold it in the air, and it falls on whatever is beneath it. This is called "dry deposition." Very small particulates or molecules of pesticide may remain in the atmosphere even when the air is relatively still. These pesticides may be removed from the atmosphere when it rains and the droplets catch them on their way down. This process is called "wet deposition",**(Li,** *et al.,* **2006).**

2.4.2 Fate and Mobility of Pesticides in Water

Water transport of pesticides can occur through wet deposition, run-off from surfaces, infiltration of water through the ground, ditches, storm

sewers, tile lines, drains, rivers, and open water currents. Water can behave much like air in terms of transporting pesticides. Water that is moving at a high velocity can carry heavier pesticides, or particles that pesticides may be attached to, then water that is moving slowly. Faster moving water also has the potential to move pesticides farther. Pesticides in open water systems may float on the water, diffuse into the water, or deposit onto the sediments at the bottom of the water body. Pesticides that move from the ground surface through the soil may reach shallow ground water or deeper aquifers,**(Yuzhou and Minghua, 2009).**

Many factors govern the potential for groundwater or surface water contamination by pesticides. These factors include: properties of the soil, properties of the pesticides, hydraulic loading on the soil, and crop management practices,**(Manuel,** *et al.,* **2008).**

2.4.3 Fate and Mobility of Pesticides in Soil

Once a pesticide is in the soil it will most likely follow one of three pathways. It will move through the soil with water, attach to soil particles, or be metabolized by organisms in the soil. Soil texture (percent sand, silt, and clay) and structure plays a large role in the transport processes of pesticides. Soils that are very sandy will allow water to move through them quickly, do not attach easily to pesticides, and generally do not contain a large population of soil organisms relative to other soil types. Soils that are high in clays and organic matter will slow the movement of water, attach easily to many pesticides, and generally have a higher diversity and

population of soil organisms that can metabolize the pesticide,**(Kohne,** *et al.,* **2009).**

Pesticide leaching below the root zone has been demonstrated in sandy as well as in loamy soils. Particularly in loamy soils, there is evidence that even strongly adsorbing chemicals can move along preferential flow pathways and that the travel times of pesticides are comparable to those of conservative solutes.

The amounts of pesticides leached below the root zone by worst case rainfall events depend on the chemical properties and can reach up to 5% of the applied mass. When there is no heavy rainfall shortly following application of chemicals, the mass annually leached below the root zone is in the range of 0.1 to 1%, occasionally it can reach up to 4%. Although a direct comparison cannot be made, the mass lost by leaching seems generally to be smaller than that lost by runoff, depending of course on the slope of the fields. Several factors that affect pesticide leaching, such as surface preparation, soil structure, soil water content, type of irrigation, pesticide formulation, time of application and rainfall events,**(Flury, 1996).**

2.4.4 Fate and Mobility of Pesticide in Organisms

There are pesticides that can accumulate in the tissues of organisms. This process is called bioaccumulation. Generally, bioaccumulation results in higher concentrations of a chemical as one goes further up the food chain. Pesticides that bio accumulate in organisms are often very persistant in the environment. They do not "break down" easily and retain their form even when ingested and stored in the body. Most pesticides that have these

characteristics have been banned from use in the United States of America, though such pesticides that were used historically are still present in the environment,**(Steen and Sven, 2000).**

The bioconcentration of pesticides and other chemicals into aquatic organisms mainly proceeds by passive diffusion through gills, epithelial tissues, or the gastrointestinal tract. Bioconcentration is primarily controlled by the physico-chemical properties of the chemicals involved, the physiological disposition of each organism, and the surrounding environmental conditions,**(El-Amrani, *et al.,* 2012).**

Pesticide residues build up in organisms and in food webs. Bioaccumulation can occur if residues build up faster than the organism can break them down and excrete them. Bioaccumulation in aquatic animals where the pesticide is taken in from the water is called bioconcentration. If a predator eats many plants and/or animals that have pesticide residues in their tissues, the predator may suffer from even greater exposure than the prey. Bald eagles, ospreys and peregrine falcons were brought to the brink of extinction because their food sources (fish and other birds) were contaminated with DDE, the breakdown product of the insecticide DDT. The residues built up with each link in the food chain until very high concentrations were present in the eagles , falcons, and ospreys. When residues increase in the food web the process is called biomagnification. No single exposure for either the prey or the predator is likely to cause injury, but the overall effects can be very harmful,**(Smital, *et al.,* 2004).**

2.5 Imidacloprid

2.5.1 Definition and Uses

Imidacloprid is an insecticide active ingredient used to control sucking insects, such as aphids, leafhoppers, psyllids and beetles in agricultural crops and turfgrass, as well as domestic pests such as fleas and cockroaches. It is most commonly applied as a soil and foliage treatment, and as a seed dressing. Crops to which this compound is applied include: various grains, maize, fruits, vegetables, potatoes, hops and turf. Imidacloprid is water soluble, persistent in soil and relatively non-volatile under field conditions. Imidacloprid is not expected to bioaccumulate. Imidacloprid residues may be measured in water and soil using High Performance Liquid Chromatography (HPLC), or gas chromatography-mass spectrometry(GC-MS),**(Capowiez, *et al.,* 2006).**

Imidacloprid is a nicotinoid neurotoxin that acts by irreversibly blocking acetylcholine receptors. Although mammals and insects both have acetylcholine receptors that can be blocked by imidacloprid, insects are more sensitive than mammals. Symptoms of imidacloprid poisoning include staggering, trembling, immobility and lethargy. Sensitivities of non-target organisms to imidacloprid varies. Imidacloprid may be highly toxic to beneficial insects, such as the honeybee and it is recommended that imidacloprid application be limited in areas frequented by honeybees. Imidacloprid may also induce toxicity in aquatic invertebrates and juvenile fish at low levels and is considered acutely toxic to birds. Moderate concentrations of the insecticide may decrease growth of algae. Phytoxicity

is not predicted for crops if the insecticide is applied post-emergence,(**Tisler,** *et al.,* **2009).**

Imidacloprid is an agonist of the nicotinic acetylcholine receptor (nAChR) at the neuronal and neuromuscular junctions in insects and vertebrates. It is structurally and functionally related to nicotine. The toxicity of imidacloprid is largely due to interference of the neurotransmission in the nicotinic cholinergic nervous system. Prolonged activation of the nAChR by imidacloprid causes desensitization and blocking of the receptor, and leads to in coordination, tremors, decreased activity, reduced body temperature and death. Presently, there is no specific antidotes, which acts as an antagonist to the effects imidacloprid, (**Deglise,** *et al.,* **2002).**

In the environment, the principal routes of dissipation for imidacloprid are aqueous photolysis, microbial degradation and uptake by plants. Imidacloprid is currently listed by the department of pesticide regulation (DPR) as a potential ground water contaminant, based on its high solubility in water, mobility and persistence in soil. The major degradation product of imidacloprid in the environment is desnitro-imidacloprid, (**Gupta,** *et al.,* **2008).**

2.5.2 Chemical and Physical Properties of Imidacloprid

Imidacloprid has the molecular formula $C_9H_{10}ClN_5O_2$ (Figure 1.2), with a molecular weight of 255.7 g/mol (Table 1.4). In appearance, it consists of colorless crystals. The insecticide is quite water soluble even at the lowest solubility value reported (510 mg/L) and could potentially leach to groundwater or be transported in runoff. In the literature, some variation

exists in reported vapor pressures for imidacloprid (Table 1.4), likely as a result of differences in the formulation of the imidacloprid-containing products. However, according to the comparatively low vapor pressure values , imidacloprid would be relatively non-volatile under field conditions. Imidacloprid did not dissociate when titrated with either acid or base. The octanol / water partition coefficient (log K_{ow}) of imidacloprid is 0.57, would not accumulate in aquatic biota, **(El-Hamady, et al., 2008).**
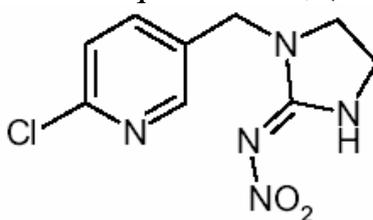
Figure 2.2 Structural Formula of Imidacloprid

Table 2.1. Physical-Chemical Properties of Imidacloprid(Fossen, 2006)

Physical- chemical property	Imidacloprid
Molecular weight	255.7
Water solubility	514 mg/L (20ºC at pH 7)
Vapor pressure	1.00×10^{-7} mmHg (20ºC)
Hydrolysis half-life	>30 days (25ºC at pH 7)
Aqueous photolysis half-life	<1 hour (24ºC at pH 7)
Anaerobic half-life	27.1 days
Aerobic half-life	997 days
Soil photolysis half-life	38.9 days
Field dissipation half-life	26.5 – 229 days
Henry's constant	6.5×10^{-11} atm m^3/mole (20ºC)
Octanol-water coefficient (K_{ow})	3.7
Soil adsorption coefficient: K_d K_{oc}	0.956–4.18 132–310

2.5.3 Environmental Fate and Behavior of Imidacloprid

2.5.3.1 Fate of Imidacloprid in Air

Imidacloprids low vapor pressure (Table 1.4) results in a very low potential for volatilization. Therefore, imidacloprid is most likely to be found in air during and immediately after spraying on crops, where it will exist primarily as an aerosol, with very little occurring in a gaseous state. Imidacloprid is rapidly photodegraded and transformed by photochemical radicals and therefore is not likely to persist in air,**(Krohn and Hellpointner, 2002).**

2.5.3.2 Fate of Imidacloprid in Soil

The dissipation time, DT50 for imidacloprid (the time required for half of it to dissipate) is in the order of 1-2 years,**(Gupta, *et al.,* 2008).** Persistence of imidacloprid in soil is affected by various factors, including temperature, organic matter of the soil, and whether the field is cropped or not. The time required for 50% of the field-applied imidacloprid to dissipate (DT50) can range any where from approximately 80 days to 2 years.

Adsorption is the main fate process for imidacloprid in soil. Imidacloprid has a medium to high sorption tendency for soil. Sorption intensity for imidacloprid and its metabolites is influenced by soil type and depends largely on organic carbon content. Soil sorption is also influenced by the soil: solution ratio. For instance, imidacloprid exhibits lower sorption behavior when the soil contains a higher water content due to its high solubility. At higher initial concentrations of imidacloprid, sorption is low

and desorption is high, therefore there is a greater potential for mobility with increasing concentration,**(Cox, *et al.,* 1997).**

Based on the high water solubility of imidacloprid (Table 1.4) and its persistence considers imidacloprid to have high leaching potential. Imidacloprid can leach to depth of at least 105 cm when irrigation conditions are unmatched to water evapotranspiration rates so that the soils become saturated or near-saturated,**(Felsot, *et al.,* 1998).**

2.5.3.3 Fate of Imidacloprid in Water

The persistence of imidacloprid in the aqueous environment depends on environmental factors including exposure to light, pH, temperature and microbial community, in addition to application rate and formulation.

 Imidacloprid exhibits an aqueous photolysis half-life of approximately 4 hours, taking into consideration variable light frequencies over the course of a day,**(Tomlin, 2000).** Imidacloprids major photolysis breakdown products in water are 6-chloro-nicotinaldehyde, 6-chloro-N-methylni-cotinacidamide, 6-chloro-3-pyridyl-methylethylendiamine, imidacloprid urea, 6-hydroxynicotinic acid, and a minor breakdown product is imidacloprid guanidine,**(Huanan, *et al.,* 2010).** The state of 6-chloro-3-pyridyl-methylethylendiamine is the major photolysis breakdown product of imidacloprid in water, **(Wamhoff and Schneider, 1999).**

The rate of hydrolysis of imidacloprid increases with temperature. This hydrolysis has also been shown to fit a first-order kinetic relationship. The main reaction product identified as a result of hydrolysis is 1-[(6-chloro-3-pyridiny$_l$) methy$_l$]-2-imidazolidone, **(Zheng and Liu, 1999).**

Degradation rates of imidacloprid, in darkness and without microbial action, vary with pH, and half-life of imidacloprid increased with alkalinity, increasing from 36.3 days at pH 4 to 41.6 days at pH 9,(**Sarkar, *et al.,* 1999**).

2.5.4   Mode of Action of Imidacloprid

Imidacloprid is a systemic insecticide meaning that it is taken up by plants, primarily through the roots, and transported within the vascular system of the plant where it can affect plant-feeding pests. Imidacloprid acts as a nicotinic acetylcholine (Ach) agonist. It binds irreversibly to the nicotinergic receptors in postsynaptic nerves, preventing acetylcholine from binding. Imidacloprid is not degraded by acetylcholinesterase. This blockage leads to the accumulation of acetylcholine, which ultimately results in paralysis and death. It has a higher binding affinity for insect nerve receptors when compared to mammalian receptors, (**Matsuda, *et al.*, 2000).**

2.5.5 Toxicity of Imidacloprid

Imidacloprid is moderately toxic if ingested. Oral LD50 values in rats were estimated to be 450 mg/kg for both sexes in one study and 500 and 380 mg/kg in males and females, respectively in another study. In mice, LD50 values were estimated at 130 mg/kg for males and 170 mg/kg for females. Imidacloprid is very low in toxicity via dermal exposure. The dermal LD50 in rats was estimated at greater than 5000 mg/kg,(**Deepu, *et al.,* 2007**).

Imidacloprid is variable in toxicity if inhaled. The inhalation LC50 was estimated to be greater than 5323 mg/m3 for dust and 69 mg/m3 for aerosol

exposure in rats. Imidacloprid dust is considered slightly toxic but the aerosol form is highly toxic,**(Tomizawa and Casida, 1999).**

Signs of imidacloprid toxicity including drowsiness, dizziness, vomiting, disorientation and fever. A 69-year-old woman ingested a formulated product containing 9.6% imidacloprid in N-methyl pyrrolide solution. The woman suffered severe cardiac toxicity and death 12 hours after the exposure. Signs of toxicity soon after the ingestion included disorientation, sweating, vomiting, and increased heart and respiratory rates,**(Huang, *et al.,* 2006).**

A 24-year-old man who accidentally inhaled a pesticide containing 17.8% imidacloprid while working on his farm was disoriented, agitated, incoherent, sweating and breathless following the exposure. Pet owners have reported contact dermatitis following the use of veterinary products containing imidacloprid on their pets,**(Agarwal, 2008).**

2.5.6 Imidacloprid Residues

Imidacloprid applied to soil is taken up by plant roots and translocated throughout the plant tissues. Freshly cut sugar beet leaves contained 1 mg/kg imidacloprid residues up to 80 days following sowing of treated seed although residues were undetectable at harvest 113 days after sowing. In a similar study, sugar beet leaves harvested 21 days after the sowing of treated seeds contained an average of 15.2 µg/g imidacloprid,**(Utture, *et al.,* 2012).**

Researchers grew tomato plants in soil treated with 0.333 mg active ingredient per test pot, and monitored the plants and fruits for 75 days.

Plants absorbed a total of 7.9% of the imidacloprid over the course of the experiment, although absorption of imidacloprid declined with time since application,(**Alsayeda, et al., 2008).**

More than 85% of the imidacloprid taken up by the tomato plants was translocated to the shoots, and only small quantities were found in the roots.

Shoot concentrations declined towards the top of the plant. These patterns were also seen in sugar beets grown from treated seed. The tomato fruits also contained imidacloprid, although tissue concentrations were not related to the position of the fruits on the plant. Although tomato fruits contained primarily unmetabolized imidacloprid, the plants' leaves also included small quantities of the guanidine metabolite, a tentatively identified olefin metabolite, and an unidentified polar metabolite in addition to the parent compound,(**Schippers and Schwack, 2010).**

Researchers sprayed imidacloprid on eggplant, cabbage, and mustard crops at rates of 20 and 40 g/ha when the crops were at 50% fruit formulation, curd formation, and pod formation, respectively. The researchers calculated foliar half-lives of 3 to 5 days based on the measured residues. Metabolites detected in the eggplant, cabbage, and mustard plants included the urea derivative [1-(6-chloropyridin-3-ylmethil) imidazolidin-2-one] and 6-chloronicotinic acid 10 days after foliar application. Residues of 2.15-3.34 µg/g were detected in the eggplant fruit**, (Juraske, *et al.,* 2009).**

Pesticide Data Program monitored imidacloprid residues in food and published their findings in 2006. Imidacloprid was detected in a range of

fresh and processed fruits and vegetables. It was detected in over 80% of all bananas tested, 76% of cauliflower, and 72% of spinach samples. In all cases, however, the levels detected were below the U.S. EPA's tolerance levels. Imidacloprid was also found in 17.5 % of applesauce and 0.9% raisin samples, although percentage of detections were greater in the fresh unprocessed fruit (26.6% of apples sampled, and 18.1% of grapes sampled),(**Robson and Wright, 2007).**

2.6 Abamectin

2.6.1 Definition and Uses

Abamectin is a mixture of avermectins containing more than 80% avermectin B1a and less than 20% avermectin B1b. These two components, B1a and B1b have very similar biological and toxicological properties. The avermectins are insecticidal and antihelmintic compounds derived from various laboratory broths fermented by the soil bacterium *streptomyces avermitilis*. Abamectin is a natural fermentation product of this bacterium. Abamectin is an insecticide as well as an acaricide and a nematicide,(**Kaspi and parrella, 2005).**

Abamectin is used to control insect and mite pests of a range of agronomic, fruit, vegetable and ornamental crops, and it is used by homeowners for control of fire ants. Abamectin is also used as a veterinary antihelmintic. Resistance to abamectin based antihelmintics, although a growing problem, is not as common as to other classes of veterinary antihelmintics. The benzoate salt emamectin benzoate is also used as an insecticide, **(Elbetieha and Daas, 2003).**

2.6.2 Chemical and Physical Properties of Abamectin

Abamectin is a white to yellowish crystalline powder. It poses a slight fire hazard if exposed to heat or flame, and a fire and explosion hazard in the presence of strong oxidizers. It may burn but will not readily ignite. Avoid contact with strong oxidizers, excessive heat, sparks or open flame. Thermal decomposition may release toxic oxides of carbon. Workers handling abamectin should wear goggles to prevent eye contact and protective clothing to prevent prolonged skin contact**, (Ozenci,***et al.,***2011).**
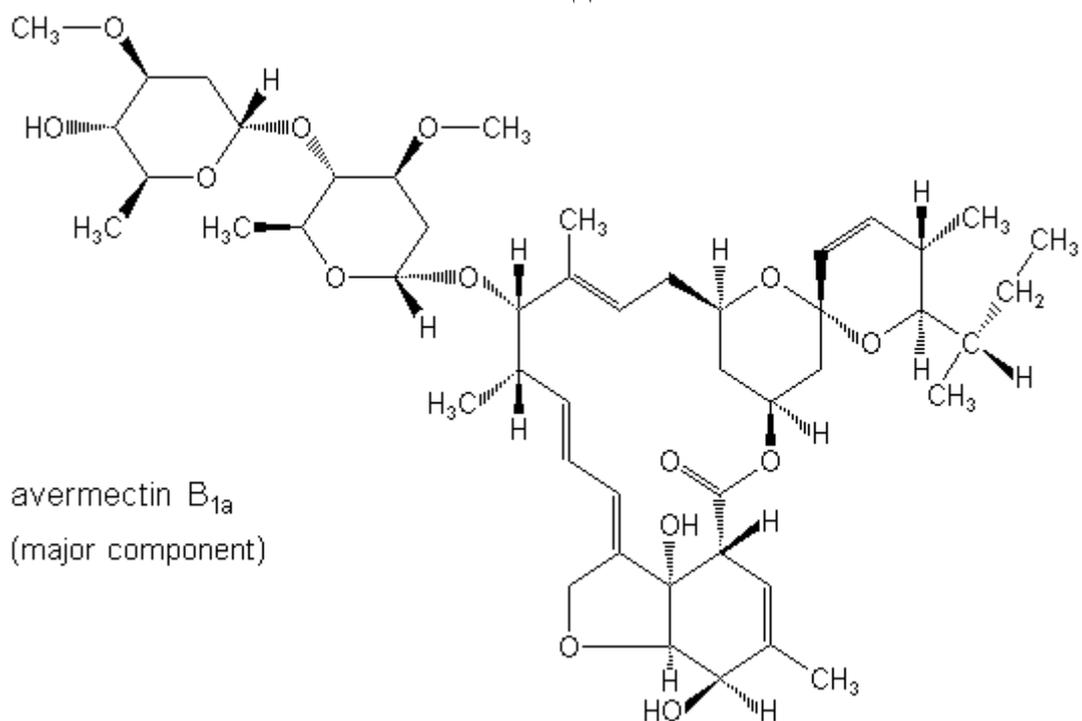
avermectin B_{1a}
(major component)
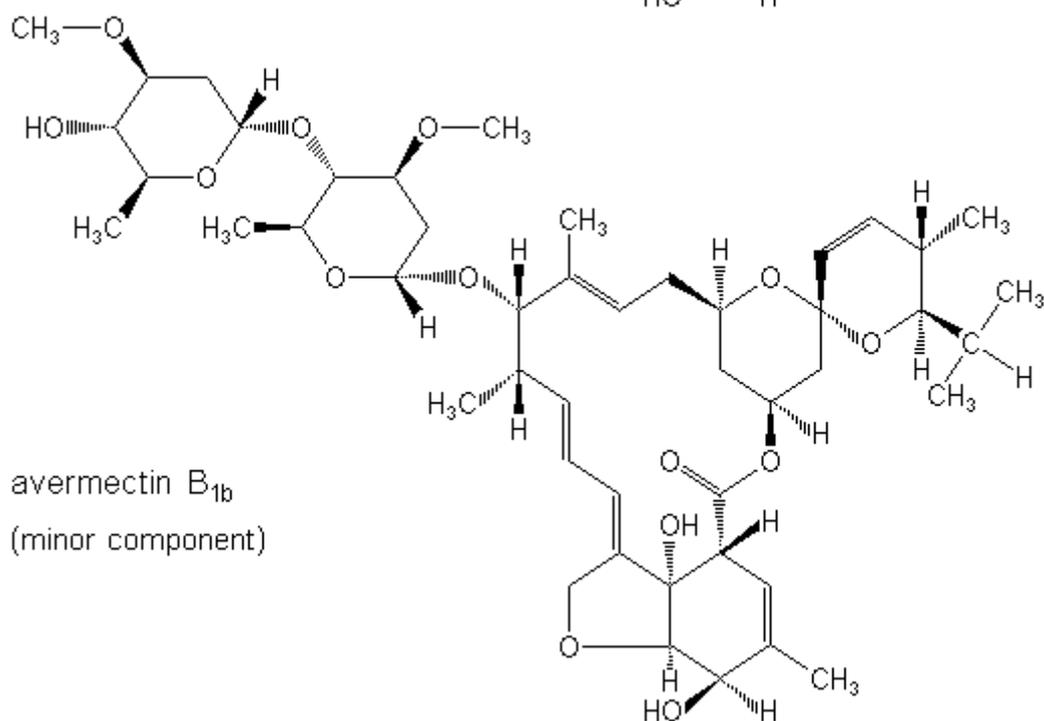
avermectin B_{1b}
(minor component)

Figure 2.3. Structural Formula of Abamectin

Table 2.2. Physical-chemical properties of abamectin (Novelli, *et al*, 2012).

Physical-Chemical property	Abamectin
Chemical name	Avermectin B1a and Avermectin B1b
Chemical Class/Use	Acaricides and insecticide; macrocyclic lactone disaccharide isolated from the soil bacterium Streptomyces avermitilis.
Density	1.16g/cm^3 at 21 ℃
Solubility in water	practically insoluble; 7.8 ppb at pH 7
Solubility in other solvents	soluble in acetone, methanol, isopropanol and toluene

2.6.3 Environmental Fate and Behavior of Abamectin

Abamectin is broken down quickly in the soil via photodegradation at the soil surface and microbial degradation in dark, aerobic conditions. The chemicals half-life is about 1 week on an unshaded soil surface and about two weeks to two months underneath the soil surface. It is also rapidly broken down in water, its half-life being four days in pond water and two to four weeks in pond sediment. Loss of abamectin from soils is thought to be due to microbial degradation. The rate of degradation was significantly decreased under anaerobic conditions. Because abamectin is nearly insoluble in water and has a strong tendency to bind to soil particles, it is immobile in soil and unlikely to leach or contaminate groundwater. Compounds produced by the degradation of abamectin are also immobile and unlikely to contaminate groundwater. When tested at pH levels common to surface and groundwater (pH 5, 7, and 9), abamectin did not hydrolyze. Abamectin is subject to rapid degradation when present as a thin film, as on treated leaf surfaces. Under laboratory conditions and in the

presence of light, its half-life as a thin film was 4 to 6 hours,(**Novelli, *et al.*, 2012).**

2.6.4 Mode of Action of Abamectin

Like most other insecticides, avermectins are nerve poisons. They stimulate the gamma-amino butyric acid (GABA) system, a chemical "transmitter" produced at nerve endings, which inhibits both nerve to nerve and nerve to muscle communication. The affected insect becomes paralyzed, stops feeding, and dies after a few days. Abamectin, used against mites and leaf-miners, is said to spare some of the major parasites of the miner and some predacious mites. When applied to foliage, it is absorbed by the leaves, where feeding insects encounter the poison,(**Borges, *et al.*, 2008).**

2.6.5 Toxicity of Abamectin

Abamectin is highly toxic to insects and may be highly toxic to mammals as well. Emulsifiable concentrate formulations may cause slight to moderate eye irritation and mild skin irritation. Symptoms of poisoning observed in laboratory animals include pupil dilation, vomiting, convulsions and/or tremors, and coma. Abamectin acts on insects by interfering with the nervous system. At very high doses, it can affect mammals, causing symptoms of nervous system depression such as in coordination, tremors, lethargy, excitation, and pupil dilation. Very high doses have caused death from respiratory failure. Abamectin is not readily absorbed through skin. Tests with monkeys show that less than 1% of dermally applied abamectin was absorbed into the bloodstream through the skin. Abamectin does not cause allergic skin reactions. The oral LD50 for

abamectin in rats is 10 mg/kg, and in mice ranges from 14 mg/kg to greater than 80 mg/kg. Rats given 0.40 mg/kg/day of abamectin had increased stillbirths, decreased pup viability, decreased lactation, and decreased pup weights. These data suggest that abamectin may have the potential to cause reproductive effects at high enough doses. Tests with laboratory animals show that ingested avermectin B1a is not readily absorbed into the bloodstream by mammals and that it is rapidly eliminated from the body within 2 days via the feces,**(Zanoli, *et al.,* 2012).**

2.6.6 Abamectin Residues

Abamectin is a mixture of avermectins B1a (80%) and avermectins B1b (20%). In sunlight the photoisomer 8,9-*Z*-avermectin is produced and becomes part of the residue. It is also described as the *D*-8,9 isomer. Avermectin B1a and 8,9-*Z* B1a produce the same fluorescent compound in the derivatization step of the analytical methods and hence a single peak on an HPLC chromatogram. Avermectin B_1b and its photoisomer 8,9-*Z*-avermectin B1b behave in the same way and appear together in a second peak in the chromatogram. Analytical methods that measure the components of the residue involve the HPLC separation and fluorescence detection of derivatives formed by converting the cyclohexene ring to an aromatic ring. Analytical methods for abamectin residues in crops, soil, animal tissues, milk and water were measured,**(Pozo, *et al.,* 2003).**

2.7 Definition of Soil

Soil is the unconsolidated mineral or organic material on the immediate surface of the earth and serves as a natural medium for the growth of land

plants. The soil is composed of particles of broken rocks that have been changed by environmental and chemical processes that include weathering and erosion. It's a mixture of minerals and organics components that are in gaseous, solid, and aqueous state. Most soils have a density between 1-2 gram\cm$_3$. Soil particles are loosely packed, forming a soil structure that filled with pore and spaces, these pores contain air (gas) and solution (liquid), as shown in following figure:

Air 25% **Mineral Matter 45%**

Organic Matter 5%

Water 25%
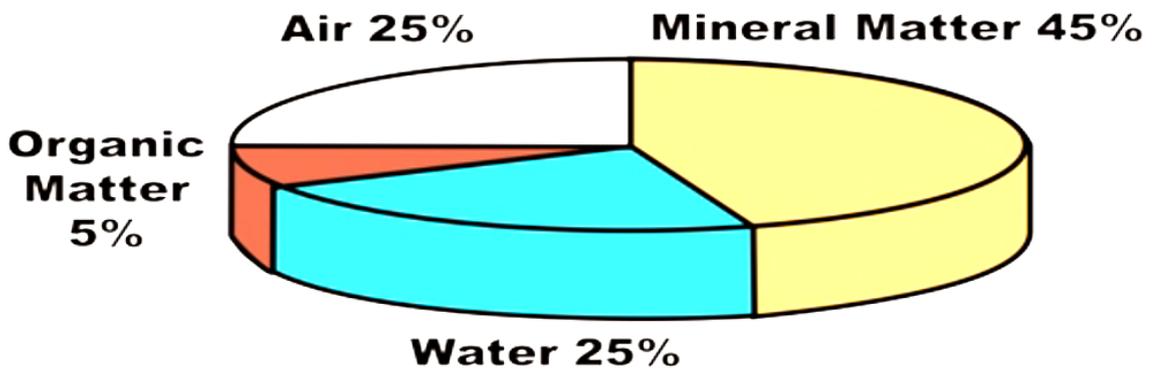
Figure 2.4: Soil structure

Most soil consists of combination of three types:

Sandy soil : particles size 0.5-2 mm, texture is gritty, compaction is low), porous, and usually holds less water for plants than other soil types, and it have the property of dryness, its particles tend to be weakly bonded together , so sandy soil easily affected by erosion.

Silt soil: particles size 0.02-0.5 mm, texture is smooth and slippery, compaction is medium, have small particles and weaker than those formed by clay particles.

Clay: a particle size less than 0.02 mm, texture is sticky, compaction is high, and have small particles that tend to bonded together strongly, can tend to hold water.

The important physical properties of soil is the pH, which controlled by the concentration of hydrogen ion in the soil. The availability of hydrogen ions in soil matrix is caused by chemical weathering reaction and by dissociation of water by action of roots.

Soil with large concentration of hydrogen ion tend to be acidic, and many of nutrients become soluble and readily leached from the soil to the ground water, but soil with low concentration of hydrogen ions tend to be alkaline so nutrients become insoluble and plant cannot extract them.

The chemicals movement(transport) processes through soil are diffusion, convection, and hydrodynamic dispersion, and chemical properties of soil like solubility, sorption, and density influence the ability of substances to be transported within soil.

More soluble chemical tend to move more easily within water than that are less soluble water, which will tend to attach to clay particles and organic matter near the soil surface,**(Staiti, 2012).**

2.8 Chemical Kinetics

2.8.1 Kinetics Experiments

Removal process can be explained by using several kinetics models. In this study both the order of the rate and the rate constants can be determined from those models. Those constants are significant for designing an

effective process. In this study we used the first and pseudo second order models**(Agrawal and Sahu, 2006).**

2.8.1.1 First Order Kinetics Model

The simple form of first order model by applying the boundary conditions, qt = 0 at t= 0 and qt = qt at t = t, is shown in Eq.(1).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

Where k_1 is the rate constant, q_e is the pesticide equilibrium concentration (mg/g); q_t (mg/g) is the amount of adsorbed pesticides at any time t(min).

2.8.1.2 Pseudo Second Order Model

The general form of the model is given as Eq.(2).

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

by integration and linearization of Eq. (3) gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

In which, k_2 is the equilibrium rate constant (g/mg.min) of pseudo-second-order chemical sorptin; q_e is the amount of adsorption sorbed at equilibrium (mg g^{-1}); q_t is the amount of adsorbate sorbed at t (min). The straight line plots of (t/q_t) vs t have been tested to obtain rate parameters**(Ugurlu *et al.*, 2008).**

Adsorption kinetics is usually controlled by different mechanisms of which the most general are the diffusion mechanisms which can be explained by intraparticle diffusion model proposed by Weber and Morris. Intraparticle diffusion model can be expressed as ,

$$q_t = k_i t^{0.5} + A \qquad (4)$$

where k_i is the intraparticle diffusion constant and the intercept A reflects the boundary layer effects. The value of k_i will be calculated from the slope of plotting q_t vs $t^{0.5}$.

2.9 Adsorption onto Soil

Adsorption phenomenon in solution systems plays an important role in many areas of practical environmental technology. In water and wastewater treatment, for example, the adsorption technique has found wide applicability because of several advantages such as high efficiency, simple operation, and easy recovery/reuse of adsorbent.

It is of general interest to understand pharmaceutical adsorption from an aqueous environment to a solid surface. The characteristics of the adsorption behavior are generally understood in terms of both equilibrium, and adsorption kinetics.

Adsorption: is the phenomenon of attraction or adhesion of solute molecules to the surface of soil particles at an interface between two phases which can be solid –liquid. The driving force for adsorption result from specific affinity of solute to the soil where the atoms at the solid surface subjected to unbalanced force of attraction , so adsorption is essentially a surface phenomenon, **(Staiti, 2012).**

Absorption: is the uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both adsorption and absorption processes take place simultaneously, the process is called sorption. Most soils absorb water and chemicals, although in amount much less than those adsorbed.

Adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption:

- Physical Adsorption or Physisorption: occur when the force of attraction existing between a dsorbate and adsorbent are weak Vanderwaal forces of attraction, Physical Adsorption takes place with formation of multilayer of a dsorbate on adsorbent. It takes place at low temperature, and its fully reversible reaction where adsorption occurs at the same temperature and the process may be slow because of diffusion effects. Molecules in the physical adsorption are free to undergo translation movement within interface.

- Chemical Adsorption or Chemisorption **:** occur when the force of attraction existing between a dsorbate and adsorbent is chemical bond, includes the transferring of electrons, as a result there is chemical bond and chemical adsorption is irreversible it takes place with formation of unilayer of a dsorbate on adsorbent. Molecules in chemical adsorption are not considered to be free to move on the surface where they attached to active center. Chemical interaction between adsorbent and a dsorbate is favored by high temperature, **(Ruthven, 2004)**.

2.10. Previous Studies:

Adsorption is integral to a broad spectrum of physical, biological, and chemical processes and operations in the environmental field. Both adsorption and desorption of the different materials in the environment can

be studied kinetically by using different equations like Freundlich and Langmuir isotherms and by knowing especial conditions like pH, time, temperature , concentration and other different condition .

Many researchers in the world and in Palestine studied the kinetics behavior and fate of may pesticides in the environment like:

<u>Cox L.,</u> et al, (1997): <u>Sorption−Desorption of Imidacloprid and Its Metabolites in Soils.</u>

Cox L. and his team studied the Sorption−desorption of imidacloprid [1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine] and meta-bolites 1-[(6-chloro-3-pyridinyl) methyl]-2-imidazolidinone (imidacloprid − urea), 1-[(6-chloro-3-pyridinyl) methyl]-4,5-dihydro-1*H*-imidazol-2-amine (imidacloprid−guanidine), and 1-[(6-chloro-3-pyridinyl)methyl]-1*H*-imidazol-2-amine (imidacloprid−guanidine−olefin) in three soils was determined using the batch equilibration technique with initial concentrations for the four chemicals ranging from 0.05 to 1.5 μg mL^{-1}, which corresponds to a field application rate of 0.2−1.0 kg ha^{-1}. Calculated slopes of the Freundlich sorption isotherms were significantly less than 1. The order of sorption (K_f) was imidacloprid−guanidine > imidacloprid−guanidine−olefin > imidacloprid > imidacloprid−urea in the three soils. Average $K_{f\text{-oc}}$ values were 203, 412, 2740, and 3200 for imidacloprid−urea, imidacloprid, imidacloprid−guanidine−olefin, and imidacloprid−guanidine, respectively. Desorption was hysteretic for all chemicals in all soils. Greatest hysteresis was observed with imidacloprid−guanidine and imidacloprid−guanidine−olefin. Sorption− desorption of imidacloprid

determined at half the solubility (250 μg mL^{-1}) ($K_{oc} = 77$) greatly overpredicts potential leaching compared to K_{oc} determined at field application rates ($K_{f\text{-}oc} = 411$), (**Cox, *et al*, 1997**).

Zhang W., et al, (2006), Adsorption Characteristics of Pesticide Abamectin in Soil Zhang W. and his team studied the adsorption characteristics of abamectin in soil. Abamectin is one pesticide widely used all over the world today, but its some important environmental behaviors, such as adsorption characteristics in soil, have not been reported until now. In order to comprehensively evaluate the environmental security of abamectin, its adsorption characteristics in four kinds of soils were studied with Freundlich equation. The results showed that in four kinds of soils, the adsorption isotherms for abamectin were all straight lines, the correlated coefficients being more than 0.9, which indicated that the adsorption was related to the distribution action of abamectin in soil organic matter. The adsorption of abamectin in humic acid was greatly stronger than that in soil, with the adsorption coefficient (Kf) being twenty-four times of that in soil, which implied that humic acid played a more important role than other factors in soil. Adsorption of abamectin in humic acid and soil increased with the decrease of solution/soil (S/L) ratio, but humic acid had more obvious influence since its stronger adsorption ability. The adsorption coefficient (Kf) in humic acid at the ratio of S/L=1∶100, was more than ten times of that at S/L=1∶20, while the adsorption coefficient (Kf) in Huajiachi soil at S/L=1∶10 was only more than twice of that at S/L=1∶5, (**Zhang, *et al*, 2006**).

In this study two pesticides were selected, imidacloprid (konfidor®) as an Insecticide and abamectin (vertimec®) as an acaricide, both the widely used in Palestine according to the results of the farmer survey which was conducted. In this research we have investigated the adsorption behavior of the two pesticides on greenhouse soil, the effect of pH, temperature, adsorbent dosage and concentration on the adsorption process using UV-Vis spectrophotometer. Results indicate the highest percentage of imidacloprid removal was 13.4 % when the adsorbent dosage 3 g soil, percentage removal of imidacloprid and abamectin increases when the concentration decreases, the maximum percentage removal reached 17 % for imidacloprid and 19 % for abamectin when their concentrations was 10 mg/L and 1 g soil, therefore, we conducted this research experiments at initial concentration 15 mg/L.

2.11 Summary

In summary to the background chapter the following was observed:

- Types of pesticides according to the target organism divided into herbicides, fungicides, insecticides, acaricides, nematicides and rodenticides.

- Agriculture in Palestine remains a dominant sector of the Palestinian economy. It represents a major component of the economy's GDP, and employs a large fraction of the population.

- Pesticides situation in Palestine as in the Arab countries is not only an issue of uncontrolled use, but it is also a problem pertaining to the handling, misuse and disposal of unwanted pesticides.

- Pesticide persistence often is expressed in terms of half-life. This is the length of time required for one-half of the original quantity to breakdown, pesticides can be divided into three categories based on half-lives: non persistent pesticides, moderately persistent pesticides or persistent pesticides.

- Imidacloprid is an insecticide active ingredient used to control sucking insects, such as aphids, leafhoppers, psyllids and beetles in agricultural crops and turfgrass, as well as domestic pests such as fleas and cockroaches. It is most commonly applied as a soil and foliage treatment, and as a seed dressing.

- Abamectin is a mixture of avermectins containing more than 80% avermectin B1a and less than 20% avermectin B1b. These two components have very similar biological and toxicological

properties. Abamectin is an insecticide as well as an acaricide and a nematicide used to control insect and mite pests of a range of agronomic, fruits, vegetable and ornamental crops.

- Soil is the unconsolidated mineral or organic material on the immediate surface of the earth and serves as a natural medium for the growth of land plants.

- Adsorption is the phenomenon of attraction or adhesion of solute molecules to the surface of soil particles at an interface between two phases which can be solid-liquid. The characteristics of the adsorption behavior are generally understood in terms of both equilibrium, and adsorption kinetics.

Accordingly this intended study to raise awareness of the issue of pesticide residues for those involved in the production, supply and marketing of the fresh produce, and to study the fate and mobility of imidacloprid and abamectin in Palestinian soil, and to understand the kinetics behind them and how they can reach groundwater. In this work removal of imidacloprid and abamectin will be conducted by adsorption onto soil. In this research we hope to make this method more efficient by understanding the factors which was affect this method.

This research was not done before in Palestine neither as project or research work. Due to environment problems arising from the trading and excessively use of agricultural pesticides by farmers and negative effects that may occur to the environment and human health, it became necessary to conduct this study.

Chapter Three

3 Methodology

The research experimental work basically depends on determining of residues of imidacloprid and abamectin versus time in soil.

Samples of soil and leachate were analyzed by UV spectrophotometer and high performance liquid chromatography (HPLC). The room temperature recorded ranged between 18 - 25 ℃. All glassware used were cleaned and dried before measurement and each measurement of this study was the average of three readings to ensure that consist values were obtained. Standard readings were obtained for imidacloprid and abamectin and were plotted against absorbance readings in order to calculate the concentrations of these compounds using calibration curves.

3.1 Materials and Methods

This chapter of study addressed on each of the tools that used to implement the experiment, method of work, and materials used in the analysis in addition to the two main pesticides which are the subject of study and the mathematical equations needed for the experimental procedures. This chapter will explain the procedure and chemicals for all experiments.

3.1.1 Chemicals and Reagents

All chemicals and solvents which used in these experiments are very pure and they where bought from Aldrich.

The following list is for all chemicals used in this study:

Imidacloprid.

Abamectin.

Distilled water.

Methanol.

Acetonitrile.

Triethylamine.

Potassium dichromate.

potassium thiosulfate.

Ferrous ammonium sulfate.

Sulfuric acid.

Diphenylamine.

Sodium hydroxide.

Hydrochloric acid.

phenolphthalein indicator**.**

ascorbic acid.

3.1.2 Instrumentation

The detecting wavelengths for pesticides residues compound were confirmed using high performance liquid chromatography (HPLC) (SHIADZU CORPORATION), with Lichoro CART$^{®}$, C18 Column (150x4.6mm,20µm) Detector FLUROCENCES ARRAY The wave lengths were 270nm and 210nm for imidacloprid and abamactin respectively.

Absorbance readings of imidacloprid and abamactine were detected using UV-VIS SHIMADZU, Model No: UV-1601 double beam spectrophotometer wavelength range from 190- 1100 nm, accuracy ± 0.004.

3.2 HPLC Scanning of Imidacloprid and Abamactine

The usual quick way to determine standard solution for imidacloprid and abamactine by high performance liquid chromatography (HPLC), The processes for detection of these compounds involve two solution preparations (mobile phase and standard solutions).

3.2.1 HPLC Scanning of Imidacloprid

For detection of imidacloprid using UV at 270 nm, chemicals and reagents (Acetonitrile solution, Triethyllamine, Distilled water and Imidacloprid were used).

In this experiment two solutions were prepared:

Mobile phase solution: solution prepared from 1 mL of triethylamine in 1600 mL of distilled water then add 400 mL acetonitrile, mix good and adjust the pH to 5.9 ± 0.1.

The standard solution: was prepared by dissolving an accurately weighed quantity of imidacloprid in diluents to obtain solution having a known concentration of about 0.0292mg/ mL.

Procedure: inject equal volume ($20\mu L$) of standard solution into HPLC to take retention time, and then inject equal volume of two sample solutions into HPLC with cleaning by mobile phase after each sample.

3.2.2 HPLC Scanning of Abamectin

For detection abamectin use UV at 210 nm, (chemicals and reagents are methanol, distilled water and abamectin).

Two solution of mobile phase and standard solutions were prepared

The mobile phase solution was prepared from methanol and distilled water(85:15 v/v) and the standard solution was prepared from 18 mg of abamactin dissolved in 100 mL methanol.

Procedure: inject equal volume (20μL) of standard solution into HPLC to take retention time and then inject equal volume of the two samples solutions into same device, with cleaning by mobile phase after each sample.

The following table showed retention time and wavelength for each pesticides.

Table 3.1. wavelength and retention time:

Pesticide Name	Wave Length(nm)	Retention Time (minute)
Imidacloprid	270	6.5
Abamectin	210	4.49

3.3 Calibration Curves for Imidacloprid and Abamectin

3.3.1 Calibration Curve for Imidacloprid

A standard calibration curves for imidacloprid and abamectin were performed by preparing diluted solution to get the concentration of 1ppm, 10ppm, 20ppm, 30ppm and 50ppm, using a control concentration of 0ppm distilled water.

A 2.857 ml of imidacloprid was placed in 1 liter volumetric flask and filled with distilled water to the mark, the concentration become 1000ppm (stock solution). A 5 mL of this stock solution to 100 mL volumetric flask and filled to the mark using distilled water, the new concentration become

50ppm. Then take 3 mL from the stock solution to 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 30ppm. After this 2 mL from the stock solution was taken and transferred to the 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 20ppm. After this 1 mL from the stock solution was taken and transferred to the 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 10ppm. After this 0.1 mL of the stock solution was taken and transferred to the 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 1ppm. Absorbance readings were recorded at 266nm for imidacloprid using UV-1601 SHIMADZU Spectrophotometer.

Table 3.2 Absorbance readings of Imidacloprid using UV-Visible Spectrophotometer at wavelength 266nm.

Concentration mg/L	Absorbance
50	3.1351
30	2.3328
20	1.5786
10	0.7687
1	0.084
0	0
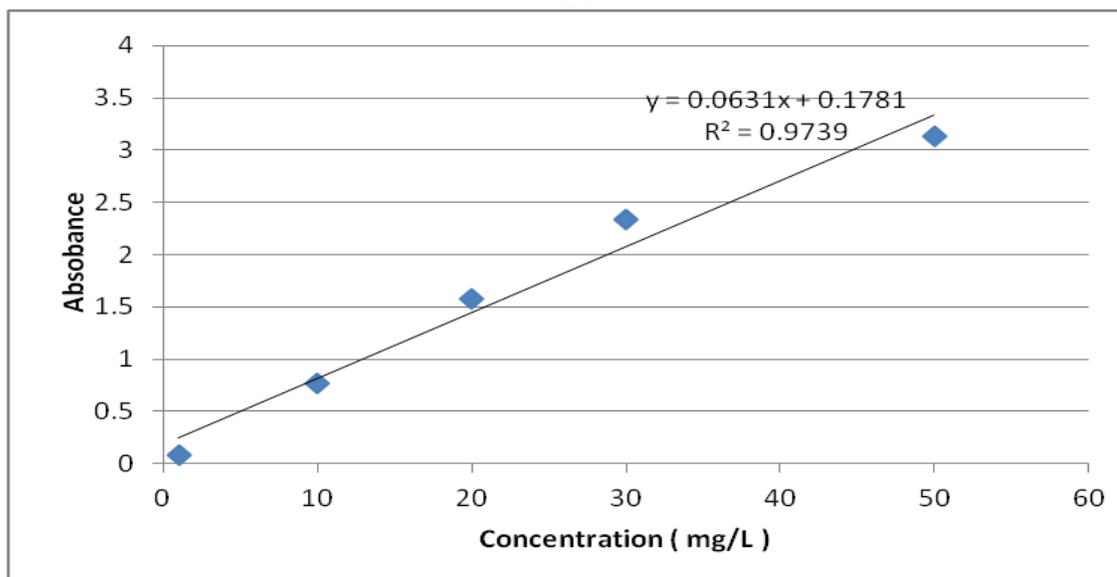
Figure 3.1: Plot of calibration curve for imidacloprid.

3.3.2 Calibration Curve for Abamectin

The calibration curve for abamectin, 55.55 mL of abamectin was placed in 1 liter volumetric flask and filled with distilled water to the mark, the concentration became 1000ppm (stock solution). A 5 mL of this stock solution to 100 mL volumetric flask and filled to the mark using distilled water, the new concentration became 50ppm. Then 3 mL from the stock solution was taken and transferred to 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 30ppm. After this 2 mL from the stock solution was taken and transferred to the 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 20ppm. After this 1 mL from the stock solution was taken and transferred to the 100 mL volumetric flask and filled with distilled water to the mark, the concentration became 10ppm. After this 0.1 mL from the stock solution was taken and transferred to the 100 mL volumetric flask and filled with distilled water to the mark, the

concentration became 1ppm. Absorbance readings were recorded at 244nm

for abamectin using UV-1601 SHIMADZU Spectrophotometer.

Table 3.3 Absorbance readings of Abamectin using UV-Visible Spectrophotometer at wavelength 244nm.

Concentration mg/L	absorbance
50	3.0679
30	2.1571
20	1.4919
10	0.7190
1	0.0588
0	0
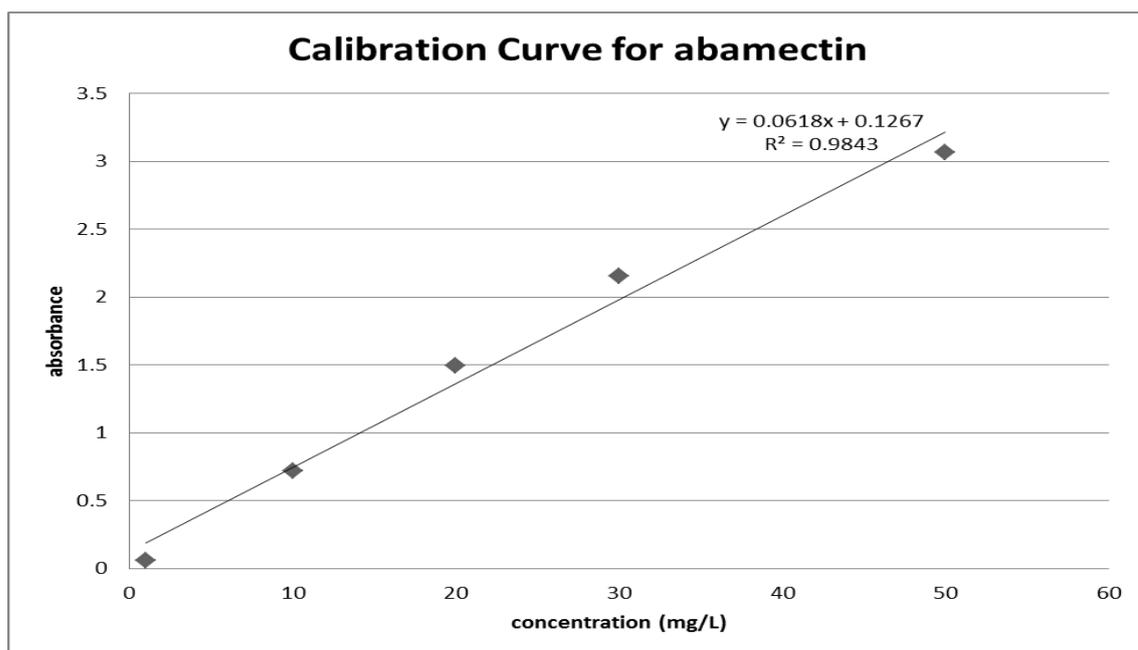
Figure 3.2: Plot of calibration curve for abamectin.

3.4 Soil Analysis

One kilogram of soil sample was weighted accurately, sieved in 2.0 mm

sieve, and dried at 105 ºC. Before any treatment with pesticides several

tests were conducted on soil as the following:

3.4.1 Soil Moisture

The results of soil analysis are to be calculated on the basis of oven dried sample weight. Therefore, the moisture analysis is executed before any other analysis. The result on basis of air-dry weight was multiplied by a moisture correction factor (Mcf), which is a ratio of the dry weight to the wet weight.

A crucible was placed in Ari J. Levy oven at a temperature of 105 ℃ for 2 hours, then cooled down to room temperature in a desiccators; the weigh of the empty crucible was recorded. A 10 g of soil sample were weighted and placed at least 12 hours in the oven at 105 ℃, then it was cooled down to room temperature in a desiccator and reweighed again. The moisture content for the soil content was calculated using the following equation:

M(moisture content)% = (B-C) / (C-A) * 100%

Where:

A: weight of empty crucible

B: sample weight + crucible weight before drying.

C: sample weight + crucible weight after drying,**(Dhyan, *et al.,* 1999).**

3.4.2 Soil pH

Add 10 g of air dried of 2 mm sieved sample into 100 mL distilled water and shake for one hour,**(Dhyan, *et al.,* 1999).**

3.4.3 Organic Carbon

The organic carbon in the sample is oxidized with potassium dichromate and sulfuric acid. The excess potassium dichromate is titrated against ferrous ammonium sulfate.

Weigh accurately 1 g of soil to contain into a dry 500 mL conical flask 10 mL 1 N $K_2Cr_2O_7$ and 20 mL concentrated H_2SO_4 were added. Immediately swirl the flask until the soil and the reagent are mixed. Insert a 200 ºC thermometer and heat while swirling the flask and the contents on a hot plate or over a gas burner and gauze until the temperature reaches 135 ºC (approximately 1/2 minute). Then 1 mL of diphenylamine indicator was added and the resulted suspension was titrated against 0.5 N ferrous ammonium sulfate solution until green color started appearing indicating the end point. The carbon content was calculated using the following equation:

Organic carbon (%) = 0.003g * N * 10 ml * (1 T/S) * 100 /ODW

$$= 3(1- T/S) / W$$

Where:

N= Normality of $K_2Cr_2O_7$ solution

T= volume of $FeSO_4$ used in sample titration (mL)

S= volume of $FeSO_4$ used in blank titration (mL)

ODW= Oven-dry sample weight (g).

% of organic matter = 1.72 * % of organic carbon, **(Walkely and Black, 1934).**

3.4.4 Soil Texture (Hydrometer Test)

The determination of the size distribution of soil particles is known as mechanical or particle size analysis. The particle size distribution of soil expresses the proportions of various size classes (clay ‹0.002 mm silt 0.002

-.0.02mm, and sand 0.02-2.0 mm particle size), represented by weight percentages of total soil, using hydrometer method, **(Bouyoucos, 1962).**

Based on the stoke Law,(the law that the force that retards a sphere moving through a viscous fluid is directly proportional to the velocity of the sphere, the radius of the sphere, and the viscosity of the fluid) ,and used to predict the settling times for various sized particles and it states that the rate which particles fall in suspension is directly proportional to their size and the force due to gravity.

The soil was sieved using 2 mm sieve, and dried at 105 ℃ for 24 hours by Elle oven, and the soil texture was determined by ASTM 152-H hydrometer device.

3.4.5 Determination of Nitrogen (Kjeldhal Test)

The soil samples is first digested in a catalyst mixture which convert all nitrogen into ammonium sulfate, then the distillation processes of ammonia (librated after sodium hydroxide is add to ammonium sulfate), over boric acid and finally the amount of the ammonia that has been trapped is determined by titration with a standard solution, and a calculation made.

145 mL of concentrated H_2SO_4 to 20g of soil, the sample was allowed to cool, and then a 50 mL of reagent (a mixture of 134 g of potassium sulfate (K_2SO_4), 7.3 grams copper sulfate $CusO_4$ catalysts solution) were added. Cool and dilute to reach one litter, store at room temperature and do not allow salt to precipitate, if precipitation does occur, put reagent bottle in warm water bath for about 30 minutes. Stir on stirrer plate until precipitation is no longer evident. Add 25mL sample of boric acid (The

boric acid captures the ammonia gas) into the mixture, forming an ammonium-borate complex (H_2BO_3). As the ammonia collects, the color of the receiving solutions changes.

The flask was placed under the condenser of distillation apparatus to separate ammonia–nitrogen from the digestate; this is accomplished by raising the pH with sodium hydroxide 50% (NaOH). This converted the ammonium (NH_4^+) ion to ammonia (NH_3).

Add an indicator to the distilled solution, and titrated with hydrochloric acid HCl "0.1 M" to the violet end point. The percent of nitrogen was calculated using the following equation:

%Nitrogen = V (HCl) xM (HCl) Mwt (N) / (V of sample *1000)*100%

N Concentration ppm = %N*10000, (**Andrew, et al., 1995**).

3.4.6 Determination of Phosphorus

Add 0.5 mL of sulfuric acid to a 10 g soil sample with 15 mL potassium thiosulfate K_2SO_4 in a 125 mL Erlenmeyer flask. Boil gently on a pre-heated hot plate for approximately 30-40 minutes. Add few drops of phenolphthalein indicator to the sample solution. Acid samples must be neutralized with 1 N sodium hydroxide (40 g NaOH/L), and get pink color, then add distilled water to volume 100ml mark and known (V1).

Take 1 mL of the mixture was added to 4 mL to phosphorus reagent that consist of 0.132 g ascorbic acid were dissolved in 25mL distilled water), then continue the volume to 25 mL (V2). If color is blue this indicates for the presence of phosphorus. A blank test shall be carried out in parallel by

the same procedure, using the same quantities of reagent (4mL) and (25mL) distilled water sample.

By using spectrophotometer at 880 nm wavelength to measure the concentration of phosphorus.

The concentration of phosphorus can be calculated by using the following equation:

Conc. of phosphorus in ppm = $(C*V 0 *V2)/ (V1*1000ml) *100$

Where:

C: Conc. that measured by UV.

V1:100ml

V2:25ml, (**Taylor, 2008**).

3.4.7 Determination of Heavy Metals

The analysis for trace heavy metal contamination is an important step in ensuring human and environmental health. Spectrophotometric method is the most important for determining heavy metals in soil. In comparison with atomic emission spectroscopy, atomic absorption spectroscopy and similar techniques, it offers the advantage of having calibration graphs that are linear over a wider range.

The heavy metals analyzed in this study included cadmium, chromium, nickel and zinc using atomic absorption flame emission spectrophotometer instrument**.**

This served as the stock solution equivalent to 100 ppm. Subsequently lower concentrations of 1 ppm, 2 ppm, 4 ppm and 6 ppm, were prepared

from the stock by serial dilution. The same method was adopted for Cr, Cd, Ni and Zn, (**Andrew, *et al.,* 1995).**

3.5 Farmer Survey

 The objective of the survey is to identify more of pesticides used in the study area, and if the farmers use the recommended quantities of pesticides. After answering the questioner, it look like most farmers are using imidacloprid (Konfidor®) for used the insecticides, and abamactin (Vertimek®) for used acaricides.

3.6 The Effect of Contact Time on Imidacloprid and Abamectin – Soil Adsorption

3.6.1 The Effect of Contact Time on Imidacloprid-Soil Adsorption

The purpose of this task is to determine the effect of contact time on the process of hydrolysis and adsorption of imidacloprid onto soil.

Stock solution of imidacloprid (1000 mg\L) were used as a dsorbate and solution of 15 ppm (50 mg\L) concentration were obtained by diluting the stock solution with distilled water.

On this experiment for imidacloprid, 15 ppm was prepared from stock solution (1.5 mL of imidacloprid solution to 100 mL volumetric flask and filled with distilled water to the mark), then we prepared 7 bottles of 330 mL in size, and we put on each bottle 50 mL of 15 mg/L solution and was mixed with 1.13 gram of oven dried sieved soil, and the pH was adjusted to 4 at 25 ℃. The adsorbent and a dsorbate suspension were separated by shaking about 15 minutes and by centrifugation at 3000 rpm for 10 minutes using Hermel Z200A centrifuge. Then the supernatants were filtered

through filter paper and the concentrations were analyzed using UV-1601 PC, SHIMADZU spectrophotometer at different time (10, 30, 60, 90, 150 minutes, 20, 24 hours) to show the effect of contact time of their uptake by the adsorbent (soil).

To determine the concentrations of imidacloprid that adsorbed on soil by subtracted the concentration in the supernatant solution from the origin one (15 ppm) then plotted graphs of imidacloprid percent removal versus time intervals. Finally plot the curve as time on X-axis and the percent removal Y-axis, **(Sruchi, 2011).**

3.6.2 The Effect of Contact Time on Abamectin – Soil Adsorption

The purpose of this task is to determine the effect of contact time on the process of hydrolysis and adsorption of abamectin onto soil.

Stock solution of abamectin (1000 mg/L) were used as a dsorbate and solution of 15 ppm (15 mg/L) concentration were obtained by diluting the stock solution with distilled water.

On this experiment for abamectin, 15 ppm was prepared from stock solution (1.5 mL of abamectin solution to 100 mL volumetric flask and filled with distilled water to the mark), then we prepared 7 bottles of 330 mL in size, and we put on each bottle 50 mL of 15 mg/L solution and was mixed with 1.13 gram of oven dried sieved soil, and the pH was adjusted to 4 at 25 ℃. The adsorbent and a dsorbate suspension were separated by shaking about 15 minutes and by centrifugation at 3000 rpm for 10 minutes using Hermel Z200A centrifuge. Then the supernatants were filtered through filter paper and the concentrations were analyzed using UV-1601

PC, SHIMADZU spectrophotometer at different time (10, 30, 60, 90, 150 minutes, 20, 24 hours) to show the effect of contact time of their uptake by the adsorbent (soil).

To determine the percentage of abamectin that adsorbed on soil by subtracted the concentration in the supernatant solution from the origin one (15 ppm) then plotted graphs of abamectin percent removal versus time intervals. Finally plot the curve as time on X-axis and the percentage removal Y-axis.

3.7. The Effect of Adsorbent Dosage of Imidacloprid and Abamectin

3.7.1 The Effect of Adsorbent Dosage of Imidacloprid

On this experiment different amounts of soil (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 g) were placed into bottles, then solution of 50 ml of 15 ppm of imidacloprid were added to each bottle and the pH was adjusted to 4. the mixtures were then shaken for 15 minutes at 25 ℃.

Centrifuging the samples, filtering them using Whatman filter paper " no. 42 " and measuring the concentration of imidacloprid using spectrophotometer.

3.7.2 The Effect of Adsorbent Dosage of Abamectin

On this experiment different amounts of soil (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 g) were placed into bottles, then solution of 50 ml of 15 ppm of abamectin were added to each bottle and the pH was adjusted to 4. the mixtures were then shaken for 15 minutes at 25 ℃.

Centrifuging the samples, filtering them using Whatman filter paper " no. 42 " and measuring the concentration of abamectin using spectrophotometer.

3.8 The Effect of pH on Imidacloprid and Abamectin-Soil Adsorption

3.8.1 The Effect of pH on Imidacloprid – Soil Adsorption

The following experiments were done:

15 ppm of imidacloprid was taken and mixed it with 1.13 gram of the soil sample and use 0.1M HCl to acidify the solution be sure the final pH is about "1.5". The same thing but changed the pH to "2.5". Then have it at 7, then use NaOH 0.1M to have it 9. The same thing but changed the pH to 12. keep in mind the concentration stays 15 ppm. Then it was shaken for 15 minutes and keep the temperature at 25 ℃.

 Centrifuging the samples, filtering them using Whatman filter papers " no. 42 " and measuring the concentration of imidacloprid using spectrophotometer, plot the curve as pH on X-axis and the percentage removal in Y-axis,(**Hari,** *et al.,* **2005)**, the results will shown in chapter four.

3.8.2 The Effect of pH on Abamectin – Soil Adsorption

The following experiments were done:

15 ppm of abamectin was taken and mixed it with 1.13 gram of the soil sample and use 0.1M HCl to acidify the solution be sure the final pH is about "1.5". The same thing but change the pH to "2.5". Then have it at 7, then use NaOH 0.1M to have it 9. Do the same thing but changed the pH to

12. Keep in mind the concentration stays 15 ppm. Then it was shaken for 15 minutes and keep the temperature at 25 ℃.

Centrifuging the samples, filtering them using Whatman filter papers " no. 42 " and measuring the concentration of abamectin using spectrophotometer, plot the curve as pH on X-axis and the percentage removal on Y-axis,(**Hari,** *et al.,* **2005**), the results will shown in chapter four.

3.9 Effect of Concentration of Imidacloprid and Abamectin on Soil

3.9.1 Effect of Concentration of Imidacloprid on Soil

The purpose of this experiment is to determine the effect of concentration on the adsorption of imidacloprid. So we have to do the following:

We prepared 5 bottles of 330 mL in size, and a different concentration of imidacloprid in each bottle as (50 ppm, 40 ppm, 30 ppm, 20 ppm, and 10 ppm), each bottle 50 mL of these concentrations were added to 1g of soil, and the pH was adjusted to 4. The bottles were shaken at 25 ℃ for 15 minutes.

Centrifuging the samples, filtering them using Whatman filter paper " no. 42 " and measuring the concentration of imidacloprid using spectrophotometer.

3.9.2 Effect of Concentration of Abamectin on Soil

The purpose of this experiment to determine the effect of concentration on the adsorption of abamectin. So we have to do the following:

We prepared 5 bottles of 330 mL in size, and a different concentration of abamectin in each bottle as (50 ppm, 40 ppm, 30 ppm, 20 ppm, and 10

ppm), each bottle 50 ml of these concentrations were added to 1g of soil, and the pH was adjusted to 4. The bottles were shaken at 25 ℃ for 15 minutes.

Centrifuging the samples, filtering them using Whatman filter paper " no. 42 " and measuring the concentration of abamectin using spectrophotometer.

3.10 The Effect of Temperature on (Imidacloprid and Abamectin) - Soil Adsorption

The purpose of this task is to determine the effect of temperature on the process of hydrolysis and adsorption of imidacloprid and abamectin onto soil.

3.10.1 The Effect of Temperature on Imidacloprid

Stock solutions of imidacloprid (1000mg/L) were used as a dsorbate and solution of 15 ppm (15mg/L) concentration were obtained by diluting the stock solution with distilled water.

In the kinetic experiments for imidacloprid, 15ppm was prepared from stock solution (1.5mL of imidacloprid solution to 100 mL volumetric flask and filled with distilled water to the mark) was mixed with 1 gram of oven dried sieved soil in a bottle. The adsorbent and a dsorbate suspension were separated by shaking and by centrifugation at 3000 rpm for 10 minutes using Hermel Z200A Centrifuge. Thermodynamic study of adsorption experiments were performed following the same procedure at 15 ℃, 25 ℃, 37 ℃ and 47 ℃. Then the supernatants were filtered through filter paper and imidacloprid concentration was analyzed using UV-1601 PC, SHIMADZU spectrophotometer.

To determine the concentration of imidacloprid that adsorbed on soil by subtracted the concentration in the supernatant solution from the origin one (15ppm) then plotted graph of imidacloprid concentration versus time intervals. Finally plot the curve as temperature on x-axis and the percentage removal on Y-axis, **(Sruchi, 2011).**

3.10.2 The Effect of temperature on Abamectin

Stock solutions of abamectin (1000mg/L) were used as a dsorbate and solution of 15 ppm (15mg/L) concentration were obtained by diluting the stock solution with distilled water.

In the kinetic experiments for abamectin, 15ppm was prepared from stock solution (1.5mL of abamectin solution to 100 mL volumetric flask and filled with distilled water to the mark) then mixed with 1 gram of oven dried sieved soil in a bottle. The adsorbent and a dsorbate suspension were separated by shaking and by centrifugation at 3000 rpm for 10 minutes using Hermel Z200A Centrifuge. Thermodynamic study of adsorption experiments were performed following the same procedure at 15 ℃, 25 ℃, 37 ℃ and 47 ℃. Then the supernatants were filtered through filter paper and abamectin concentration was analyzed using UV-1601 PC, SHIMADZU spectrophotometer.

To determine the concentration of abamectin that adsorbed on soil by subtracted the concentration in the supernatant solution from the origin one (15ppm) then plotted graph of abamectin concentration versus time intervals. Finally plot the curve as temperature on x-axis and percentage removal on Y-axis, **(Sruchi, 2011).**

Chapter Four

4. Results & Discussion

The results of this work are represented in tabular and graphical form. Results were devoted to understand the behavior and the fate of abamectin and imidacloprid in soil including their adsorption in soil. Discussion of the results follows each part of experimental work.

4.1. Soil Tests

Samples of red soil were collected from greenhouse and analyzed in order to evaluate the soil texture, moisture, pH value. Table "4.1" shows the results obtained from these tests.

Table (4.1): Soil pH, texture, moisture, Organic carbon and Organic matter for soil before pollution.

Soil Properties	Result
pH value	7.18
Clay (%)	43%
Silt (%)	57%
Moisture content	13.12%
Organic Carbon %	1.38%
Organic matter %	2.37%

From the table above it was noticed that the silt percentage is larger than that in the clay , organic carbon and organic matter are less than the percentage that increase the adsorption (3%, 5%) respectively ,this reduces the adsorption of pesticides. Sorption of pesticides to soil generally increases with soil organic matter content,**(Liu,** *et al***, 2006).**

4.2 Phosphorus and Nitrogen:

The concentration tests of nitrogen and phosphorus in the soil were analyzed and the results showed that the concentration of nitrogen was 4288.23 ppm, and the concentration of phosphorus was 40 ppm, the results showed that there was a significant increase in the concentration of nitrogen, because of the large number of dead organisms in the soil as well as the previous crop residues and heavily used of organic fertilizers.

4.3 Heavy metals (Cadmium, Chrome, Zinc, Nickel).

Table 4.2 Heavy metals concentrations in soil

Heavy metals	Cd conc. ppm	Cr conc. ppm	Ni conc. ppm	Zn conc. ppm
WHO standards	0.003	0.050	0.020	4.000
Results	0.0101	0.0044	0.0037	0.4691

It has been observed from table 4.3 during the examination of heavy metals in the soil that cadmium concentrations were found to be higher than the WHO acceptable maximum of 0.003 mg/L, so cadmium toxicity has been reported to cause food poisoning, mutation, hypertension, and cancer among others, long term exposure to cadmium has been found to cause serious damage to kidney, liver, bone and blood, **(Chen, *et al*., 2010),** but Zn, Ni and Cr concentrations in soil were lower than the WHO acceptable.

4.4 Farmer Survey Results

This survey consists of two parts, the first shows general information on farmers and farming practices, the second part shows characteristics of

pesticides application. After the survey distributed to fifty farmers the results we obtained in table 4.3 and 4.4.

Table 4.3: General Information on Farmers and Farming Practices.

Variable	Frequency (%) Total: 50
Type of agriculture Opened Greenhouse Plastic tunnels	 1(2.0) 48(96.0) 1(2.0)
Type of fertilizer Organic Chemical Mixture	 10(20.0) 25(50.0) 15(30.0)
Type of control (spraying) Biological Chemical Mixture	 3(6.0) 37(74.0) 10(20.0)
The most frequent insecticide used by the farmers Konfidor (imidacloprid) Dorsban Marshal	 41(82.0) 5(10.0) 4(8.0)
The most frequent acaricide used by the farmers Neoron Vertimec (abamectin) Masay	 6(12.0) 42(84.0) 2(4.0)
Times of using the insecticides during the season Twice Four times More than four times	 5(10.0) 15(30.0) 30(60.0)
Times of using the acaricides during the season Twice Four times More than four times	 6(12.0) 14(28.0) 30(60.0)

The results in table 4.3 indicate the following:

- Most farmers use greenhouses in their agriculture, which shows that farmers are willing to invest in agriculture and spend more money until they get more profits.

- 50 % of the farmers use chemical pesticides and chemical fertilizers, which may increase the likelihood of contamination by these chemicals.

- Imidacloprid and abamectin pesticides are the most frequent types used by 82 % and 84 % respectively on the study sample, so we conducted this research on these pesticides which are the most widely used in the study area by farmers.

- Most farmers using insecticides and acaricides more than four times during the season, which leads to increase the likelihood of the presence of residues of those pesticides in the soil, this was one of the reasons that made us do this study

Table 4.4: Characteristics of Pesticides Application

Variable	Frequency (%) Total: 50
Farmer age 20 – 30 years 30 – 40 years More than forty years	5(10.0) 15(30.0) 30(60.0)
Education Uneducated Bachelor Master	40(80.0) 10(20.0) 0(0.0)
House type Property Rent Other	32(64.0) 15(30.0) 3(6.0)

|	
Duration of work in agriculture	
1 – 3 years	7(14.0)
4 – 10 years	15(30.0)
More than 10 years	28(56.0)
Type of water used for irrigation	
Groundwater (wells)	29(58.0)
Surface water (pools)	21(42.0)
Duplicate sewage water	0(0.0)
The instructions on the can are read	
Yes	13(26.0)
No	24(48.0)
Other	13(26.0)
The same amount instructed by the manufacture are used	
Yes	4(8.0)
No	40(80.0)
Other	6(12.0)
The farmers use mask during preparation the pesticide	
Yes	3(6.0)
No	42(84.0)
Other	5(10.0)
The farmers use gloves during preparation the pesticide	
Yes	4(8.0)
No	44(88.0)
Other	2(4.0)
The farmers use protection eyeglasses during preparation the pesticide	
Yes	
No	3(6.0)
Other	46(92.0)
	1(2.0)
The fertilizer is added by …	
During irrigation	41(82.0)
Spraying fertilizer on the leaves of the plant	4(8.0)
Adding the fertilizer directly on the plant	5(10.0)

The results in table 4.4 indicate the following:.

- Most farmers age more than forty years, which indicates that they have extensive experience. Mostly uneducated this is one of the reasons for non use the recommended quantities.

- 64% of the farmers have their own house. 56% of them have more than 10 years experience, and 58% use groundwater (wells) for irrigation.

- 48% of the farmers do not read the instructions on the pesticide can and 80% of them do not use the same amount instructed by the manufacture, which means an increase in contamination and residues arrival to groundwater by filtration.

- Protection procedures are not followed, 84% of the farmers do not wear masks, 88% do not use gloves and 92% do not use protection eyeglasses during their work, which threatens those farmers to contamination and influence their health.

4.5 The Effect of Contact Time on Imidacloprid and Abamectin – Soil Adsorption

4.5.1 The Effect of Contact Time on Imidacloprid - Soil   Adsorption

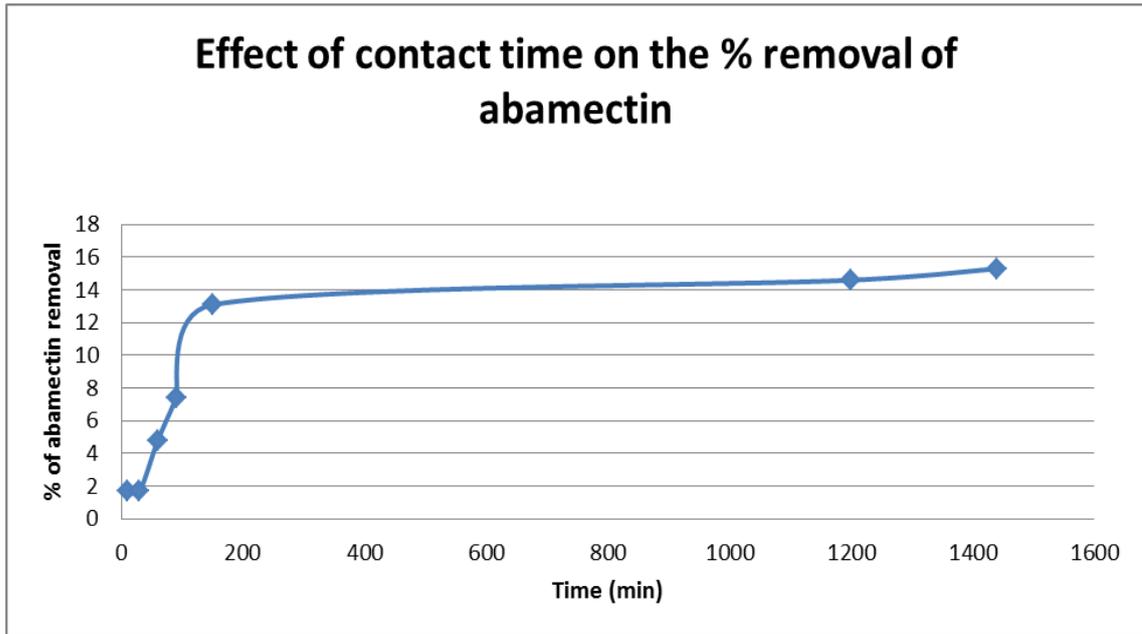Effect of contact time on imidacloprid are shown in Figure 4.1.
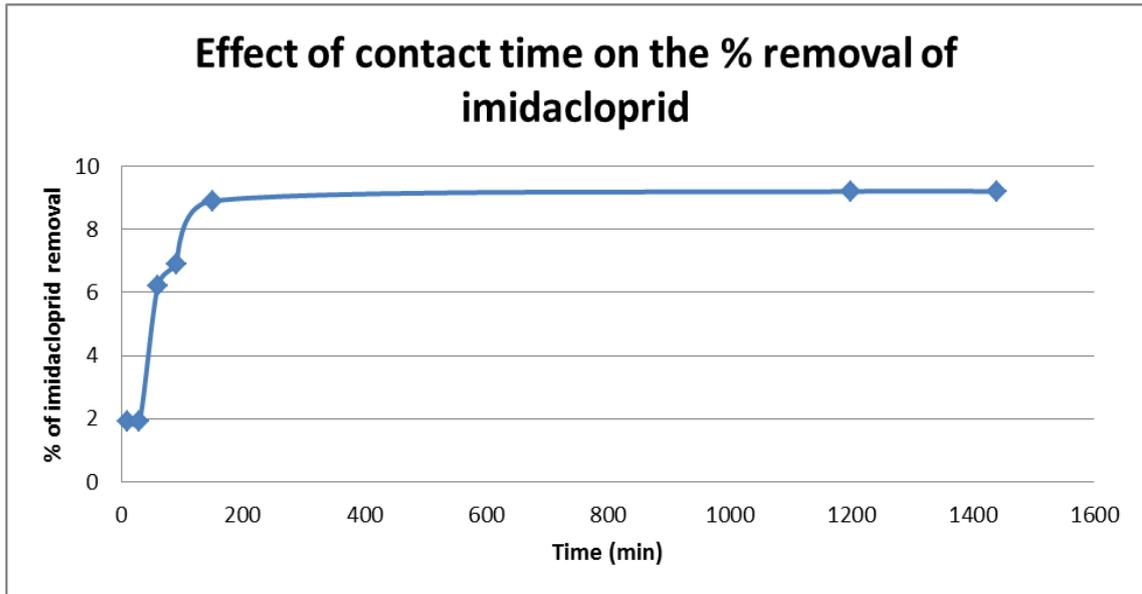
Figure (4.1), Effect of contact time on the % removal of imidacloprid by soil (initial conc.: 15 mg/L, initial pH: 4, temperature: 25 ºC, 1 g soil and contact time: 15 min).

As we see from the figure 4.1, the first half-hour has a low percent removal about 1.9 % only, but after about an hour of adsorption the percent removal rise slowly to reach 6.2 %, either after 90 minutes the percent removal has been reached 6.9 %, and after 150 minutes the percent removal was rises more to about 8.9 %, then equilibrium occurs at about 150 minutes but after 15 minutes most of the adsorption attained.

4.5.2 The Effect of Contact Time on Abamectin - Soil Adsorption

Effect of contact time on abamectin are shown in Figure 4.2.

Figure (4.2) Effect of contact time on the % removal of abamectin by soil:, (initial conc.: 15 mg/L, initial pH: 4, temperature: 25 ºC, 1 g soil and contact time: 15 min).

The figure 4.2 indicates that abamectin adsorption onto soil increases when increasing treatment time starting from "0 to 150" minutes and then becomes constant after that until about 24 hours with percentage removal 15.3 %.

4.6 The Effect of Adsorbent Dosage on Imidacloprid and Abamectin

4.6.1 The Effect of Adsorbent Dosage on Imidacloprid

The effect of adsorbent dosage on imidacloprid was studied, using

(0.5, 1.0, 1.5, 2.0, 2.5, 3.0 g soil) at an adsorption time of 15 min. The results are summarized in Figure 4.3.
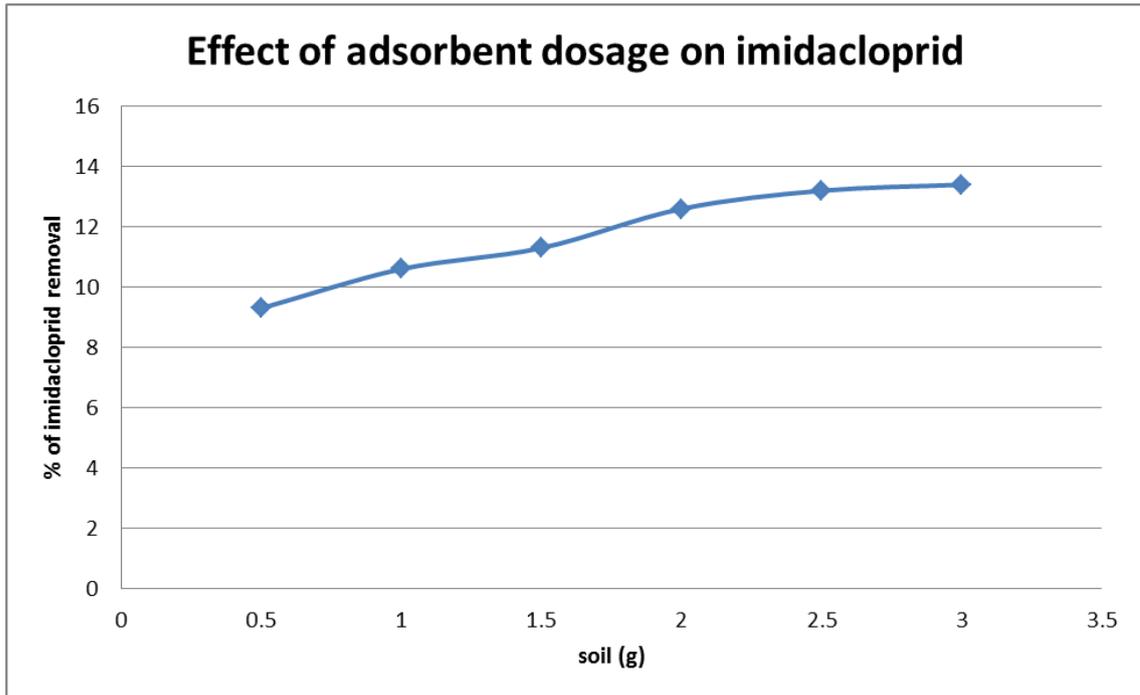
Figure 4.3: Effect of adsorbent dosage on % of imidacloprid removal at (initial conc.: 15 mg/L, initial pH: 4, temperature: 25 ºC and contact time: 15 min).

The percent of imidacloprid removal increased by increasing adsorbent dosage. Adsorption increases up to 13.4 % with adsorbent dosage of (3g/50mL), because increasing adsorbent dosage at fixed imidacloprid concentration provided more available adsorption sites and thus increased the extent of imidacloprid removal.

4.6.2 The Effect of Adsorbent Dosage on abamectin

The effect of adsorbent dosage on abamectin was studied, using(0.5, 1.0, 1.5, 2.0, 2.5, 3.0 g soil) at an adsorption time of 15 min. The results are summarized in Figure 4.4.

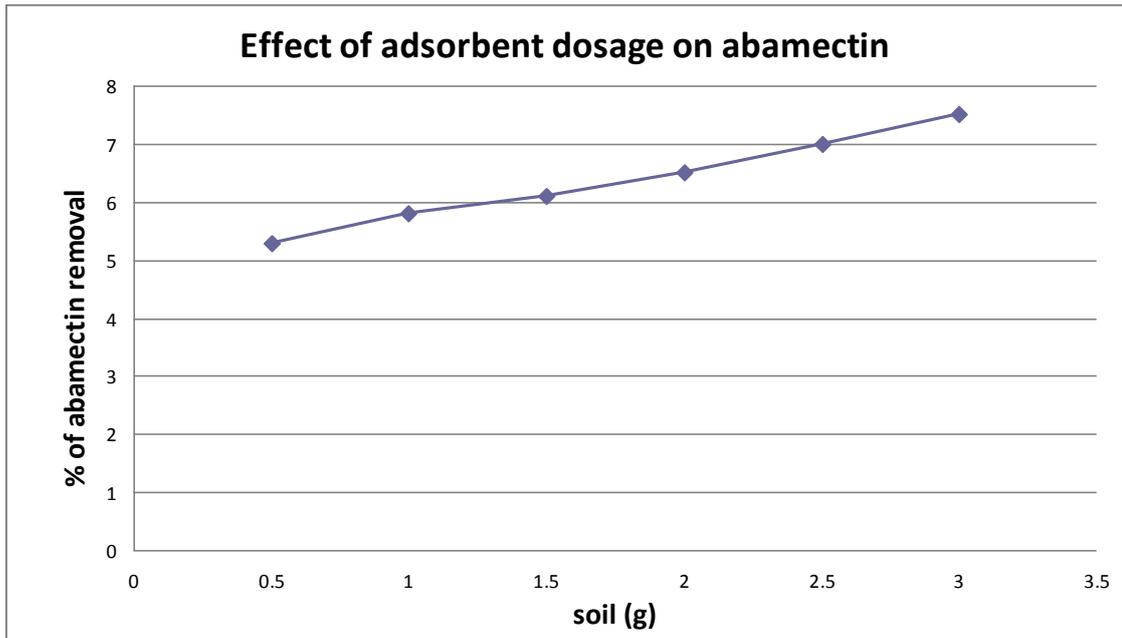**Figure 4.4: Effect of adsorbent dosage on % of abamectin removal at (initial conc.: 15 mg/L, initial pH: 4, temperature: 25 ºC and contact time: 15 min).**

As we noticed from the figure 4.4, the percent of abamectin removal increased by increasing adsorbent dosage. Adsorption increases up to 7.5 % with adsorbent dosage of (3 g /50 mL), because increasing adsorbent dosage provided more available adsorption sites and thus increased the extent of abamectin removal.

4.7 The Effect of pH on Imidacloprid and Abamectin– Soil Adsorption

4.7.1 The Effect of pH on Imidacloprid – Soil Adsorption

The extent to which adsorption was influenced by varying pesticide ionization state and aquifer material surface properties with varying pH will be shown in figure 4.5.
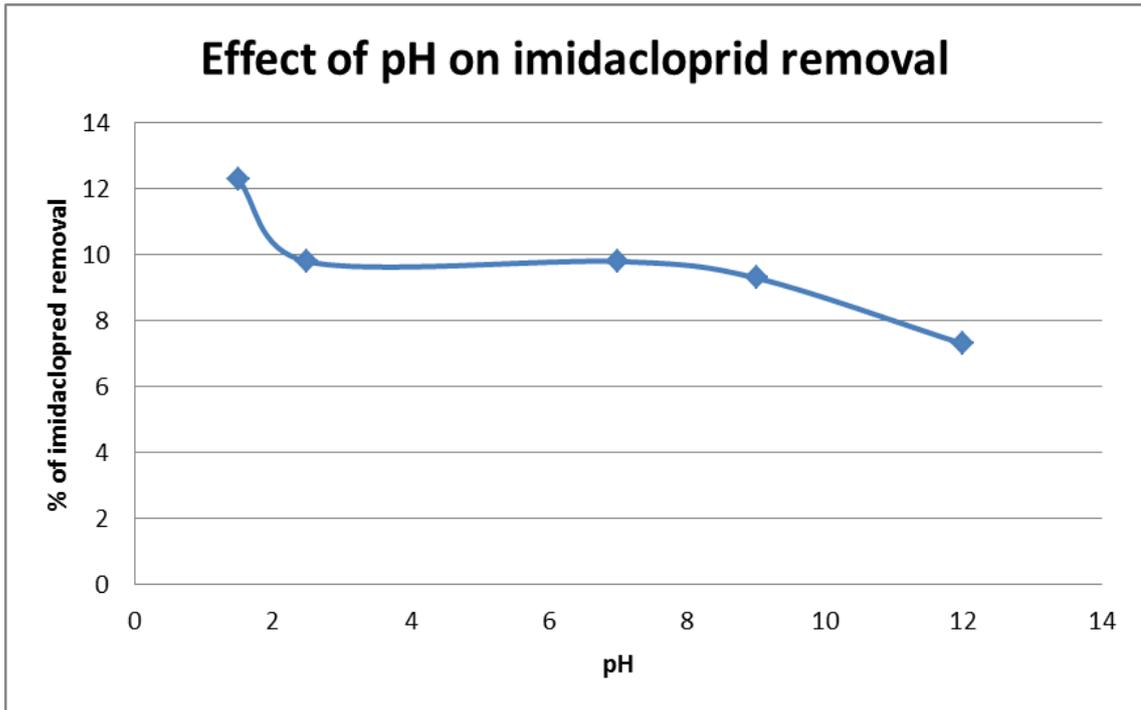
Figure (4.5): Effect of pH on imidacloprid removal at different pH, (initial conc.: 15 mg/L, temperature: 25 ºC and contact time: 15 min).

The figure shows that the amount of adsorbed imidacloprid increases at lower pH. At pH "1.5" the percent of imidacloprid removal was 12.3 %, at pH "2.5" and pH "7", the percent of imidacloprid removal was decreased from 12.3 % to 9.8 %, then as pH increases to   "9" the percent of imidacloprid removal decreased to 9.3 %, the percent of imidacloprid removal decreased rapidly at the pH "12" to 7.3 %, that indicates adsorption decreases when pH increases for imidacloprid. Imidacloprid was found to hydrolyze more rapidly in alkaline water,**(Zheng and Liu, 1999).** So hydrolysis of imidacloprid produced the metabolite 1-[(6-chloro-3-pridinyl)methyl]-2-imidazolidone**.** This may be further broken down via oxidative cleavage of the N-C bond between the pyridine and imidazolidine rings,**(Liu, *et al*, 2006).**

4.7.2 The Effect of pH on Abamectin – Soil Adsorption

The extent to which adsorption was influenced by varying pesticide ionization state and aquifer material surface properties with varying pH will be shown in figure 4.6
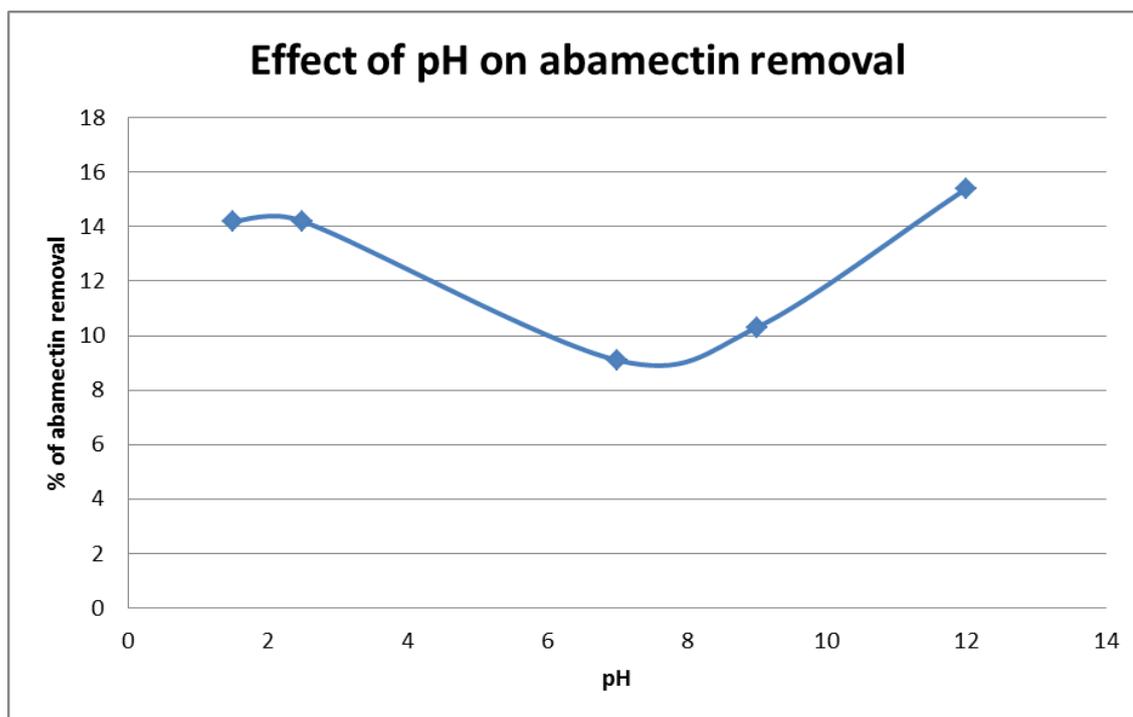

Figure (4.6) Effect of pH on abamectin removal at different pH:, (initial conc.: 15 mg/L, temperature: 25 ºC and contact time: 15 min).

As we noticed from the figure above that at lower pH "1.5" and "2.5" the percent of abamectin removal was 14.2 %, and at pH "7" the percent of abamectin removal was decreased to 9.1 %, then the percent of abamectin removal at the pH "9" increased to 10.3 %, finally the percent of abamectin removal raised rapidly at the pH "12" reached to 15.4 %.

4.8 Effect of Concentrations of Imidacloprid and Abamectin on Soil

4.8.1 Effect of Concentration of Imidacloprid on soil

The purpose of this experiment to determine the effect of concentration on the adsorption of imidacloprid. Concentration of imidacloprid was studied

using (50 ppm, 40 ppm, 30 ppm, 20 ppm, and 10 ppm) imidacloprid. The results are shown in figure 4.7.
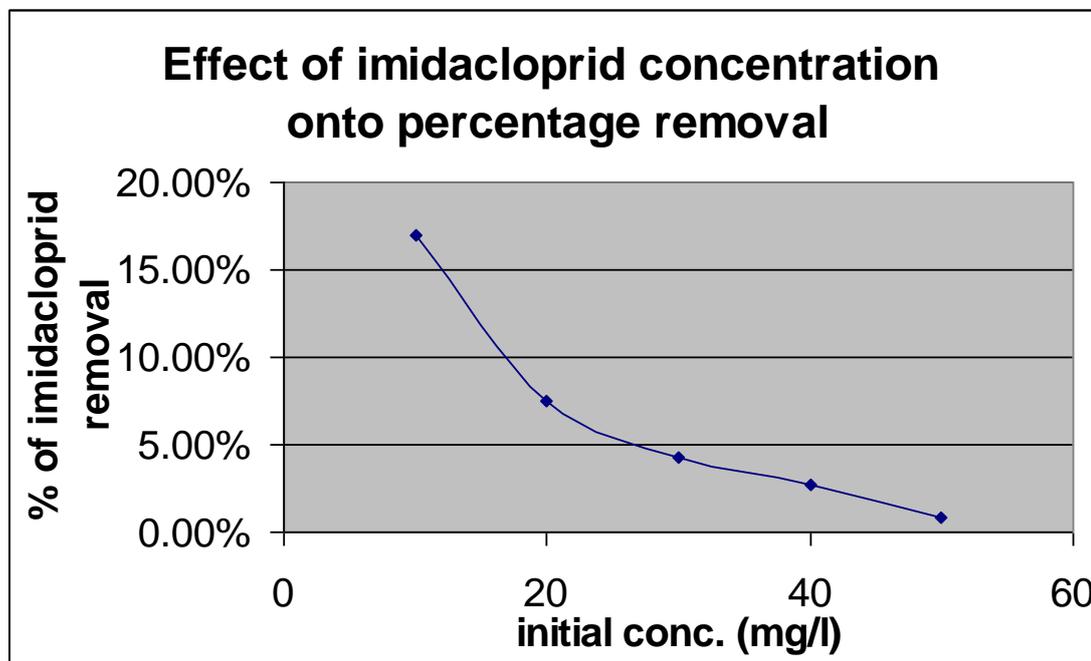
Figure (4.7): Effect of imidacloprid concentration onto percentage removal in soil at different concentrations, initial pH: 4, temperature: 25 ºC and contact time: 15 min).

From the figure 4.7 above it was noticed that when there is lower concentration the sorption became larger. Sorption-desorption is also concentration-dependent, with higher sorption rates when there is a lower initial concentration of imidacloprid present, At higher initial concentrations of imidacloprid, sorption is low and desorption is high, therefore there is a greater potential for mobility with increasing concentration **(Cox, *et al*, 1998).** Imidacloprid adsorption to soil particles increases as the concentration of the insecticide decreases,**(Kamble and Saran, 2005).**

4.8.2 Effect of Concentration of Abamectin on soil

The purpose of this experiment to determine the effect of concentration on the adsorption of abamectin. Concentration of abamectin was studied using (50 ppm, 40 ppm, 30 ppm, 20 ppm, and 10 ppm) abamectin. The results are shown in figure 4.8.
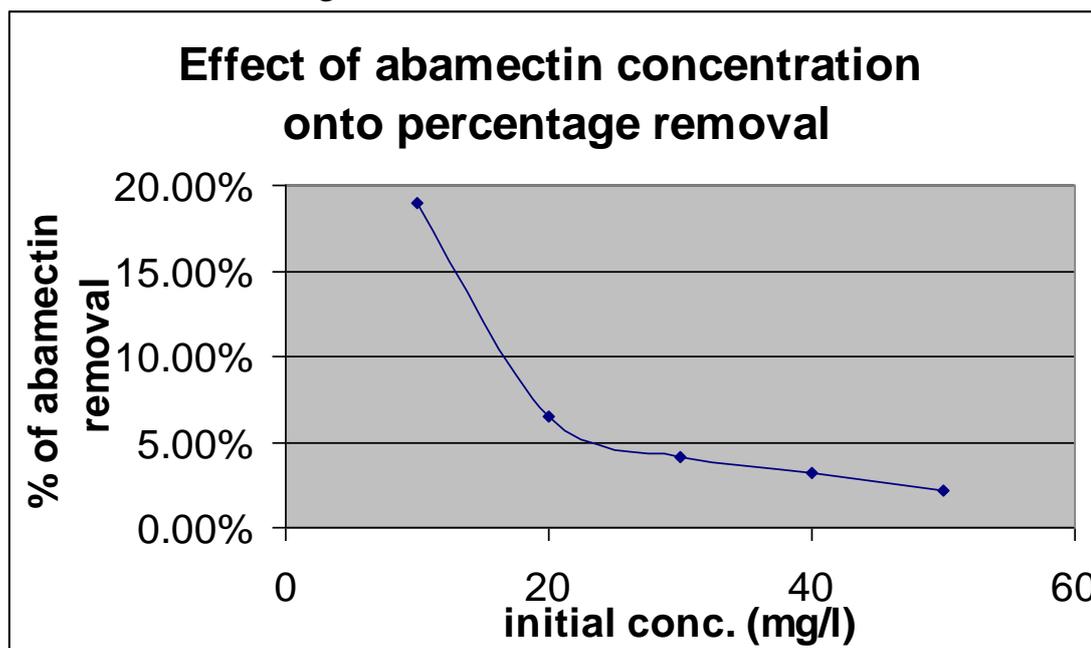

Figure (4.8): Effect of abamectin concentration onto percentage removal in soil at different concentrations, initial pH: 4, temperature: 25 ºC and contact time: 15 min).

From the figure 4.8 above it was noticed that when there is lower concentration for abamectin the sorption became larger. Sorption-desorption is also concentration-dependent, with higher sorption rates when there is a lower initial concentration of abamectin present, At higher initial concentrations of abamectin, sorption is low and desorption is high, therefore there is a greater potential for mobility with increasing concentration.

4.9 The Effect of Temperature on (Imidacloprid and Abamectin) -Soil Adsorption

4.9.1 The Effect of Temperature on Imidacloprid – Soil Adsorption

 The effect of temperature on imidacloprid adsorption onto soil was investigated in the range 15-47°C. The results are shown in Figure 4.9.
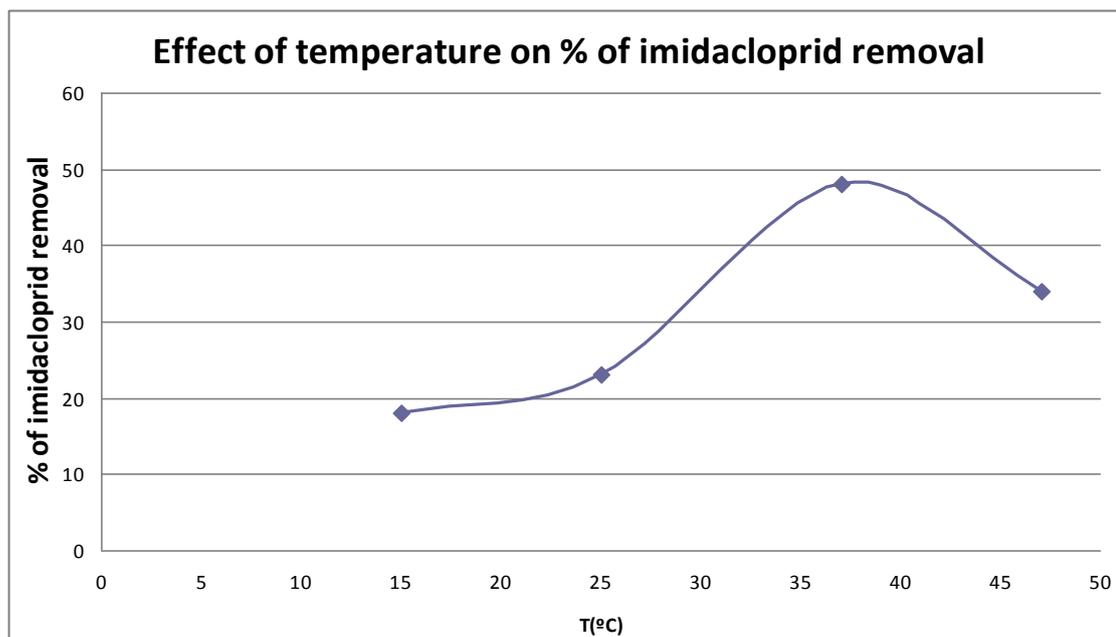
Figure (4.9): Effect of temperature on percentage removal of imidacloprid by soil at different temperature (initial conc.: 15 mg/L, initial pH: 4 and contact time: 15 min).

From figure 4.9 we notice that the percentage removal of imidacloprid increases with increasing temperature up to 37 ℃ , then return to decrease, so the optimum degree for imidacloprid removal is about 37 ℃   reached to 48% percentage removal, and at 47 ℃ the percentage removal reached about 34%.

4.9.2 The Effect of Temperature on Abamectin – Soil Adsorption

The effect of temperature on abamectin adsorption onto soil was investigated in the range 15-47 ℃ . The results are shown in Figure 4.10.
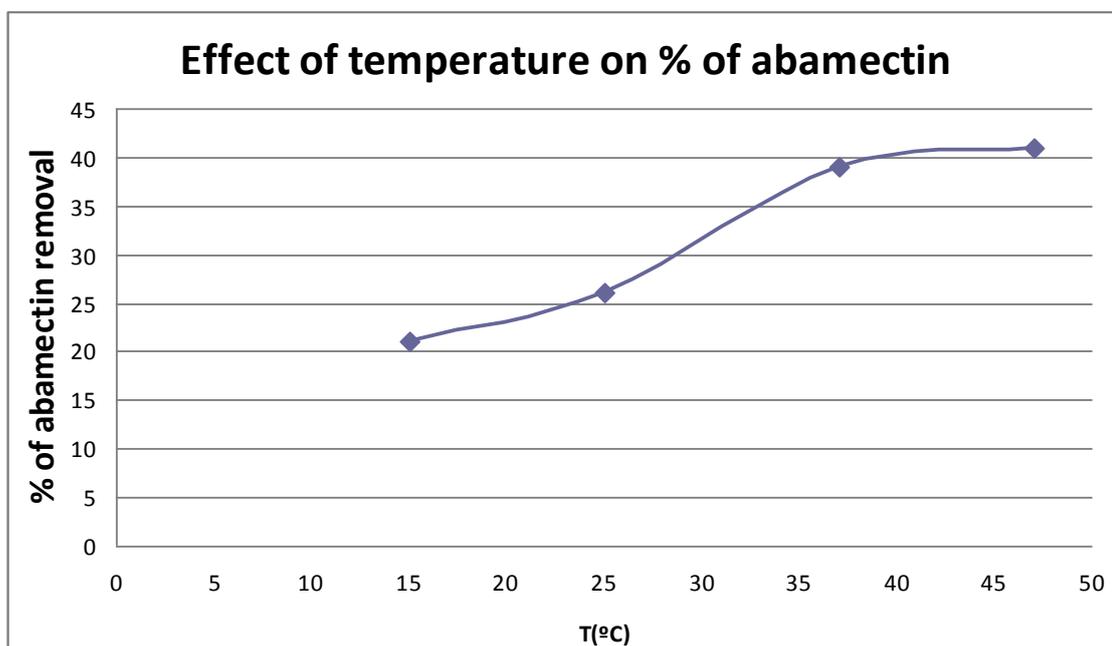
Figure (4.10): Effect of temperature on percentage removal of abamectin by soil at different temperature (initial conc.: 15 mg/L, initial pH: 4 and contact time: 15 min).

As we noticed from figure 4.10, the percentage removal of abamectin increases with increasing temperature, so the optimum degree for abamectin removal about 47 ℃ reached to 41%.

4.10 Adsorption Thermodynamics

The thermodynamic parameters including changes in standard enthalpy ($\Delta H°$), standard entropy ($\Delta S°$), and standard free energy ($\Delta G°$) of adsorption can be calculated by means of the following equations.

$$\ln K_d = \Delta S°/R - \Delta H°/RT \qquad (1)$$

Where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution temperature and K_d is the distribution coefficient which can be calculated as:

$$K_d = C_{Ae} / C_e \qquad\qquad (2)$$

where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration. $\Delta G°$ can be calculated using the relation below:

$$\Delta G° = - RT \ln K_d \qquad\qquad (3)$$

The values of $\Delta H°$ and $\Delta S°$ are calculated from the slopes and intercepts of the linear variation of ln K_d with reciprocal temperature (1/T) figure (4.11) and (4.12). The obtained thermodynamic values are given in Table 4.3.
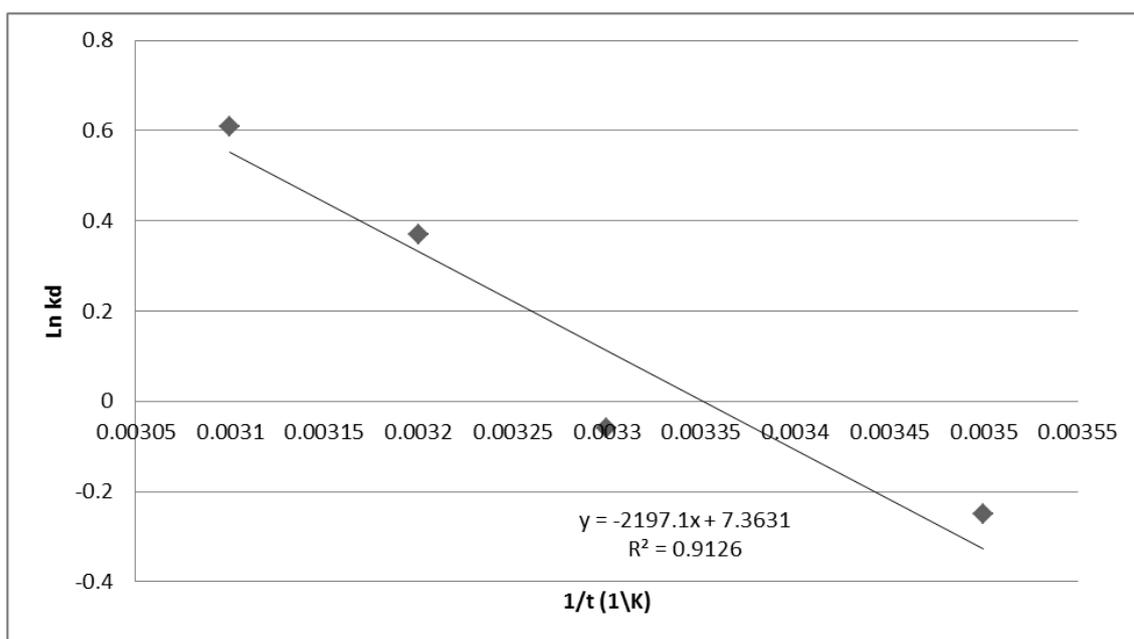
Figure (4.11): Plot of lnKd *vs*. 1/T for 15 mg/L concentration of imidacloprid.
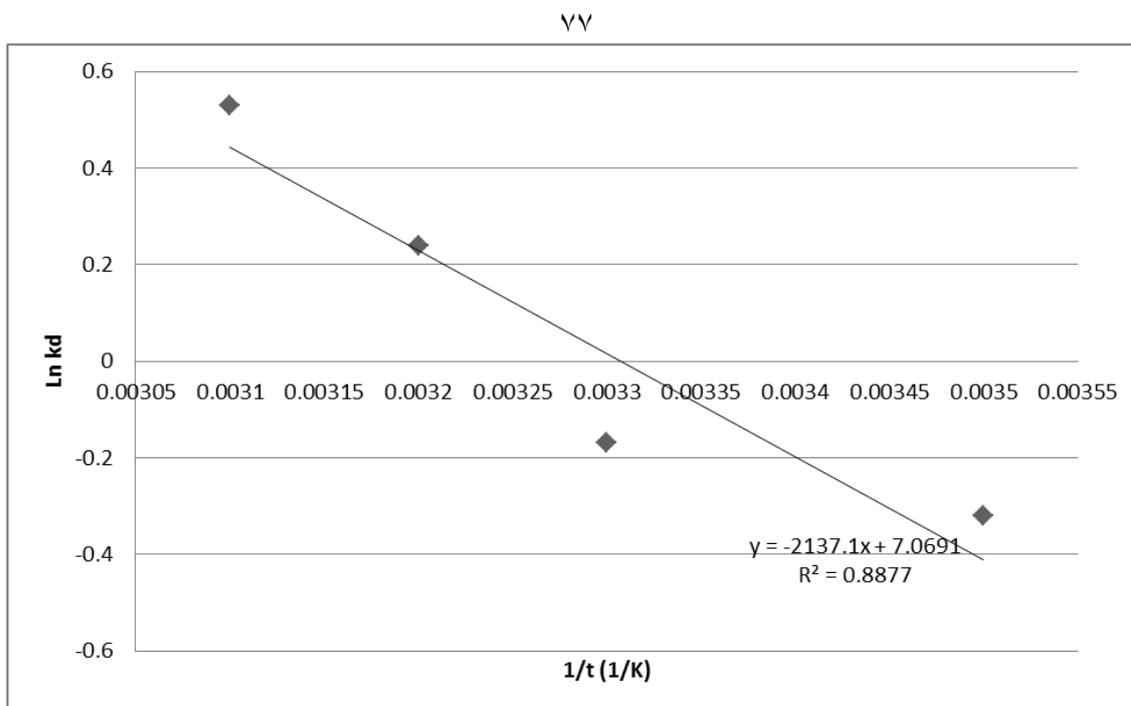
Figure (4.12): Plot of ln*K*d *vs*. 1/T for 15 mg/L concentration of abamectin.

Table 4.5 : The values of thermodynamics parameters of adsorption of pesticides on soil.

Pesticides	ΔH^O (kJ/mol)	ΔS^O (J/mol K)	ΔG^O (kJ/mol)			
			288 K	298 K	310K	320 K
Abamectin	17.7	58.7	2.68	1.39	-1.98	-4.37
Imidacloprid	18.3	61.2	2.09	0.49	-3.05	-5.03

The negative values of $\Delta G°$ at various temperatures indicated that the adsorption process on soil is spontaneous and the positive values of $\Delta H°$ show that the adsorption is endothermic. Furthermore, the positive value of entropy indicates there is no affinity of adsorbent material for pesticides. Decrease in the value of $\Delta G°$ with rise in temperature show that the adsorption is more favorable at higher temperature.

4.11 kinetic Adsorption Study

4.11.1 Pseudo first order model

First order rate constant was calculated by Equation (1).

$$\text{Log } (q_e-q_t) = \log q_e - k_1*t/2.303 \quad (1)$$

Where q_e and q_t are the amount of pesticides adsorbed (mg/L) at equilibrium and at time t (min) respectively while k_1 is the first order rate constant. Therefore first order rate constant k_1 and q_e were calculated from slope and intercept of plot log (q_e − q_t) versus t. This model was not followed by adsorption of imidacloprid and abamectin.

Pseudo first order for imidacloprid

$$y = -0.0056x + 0.5114$$
$$R^2 = 0.9239$$
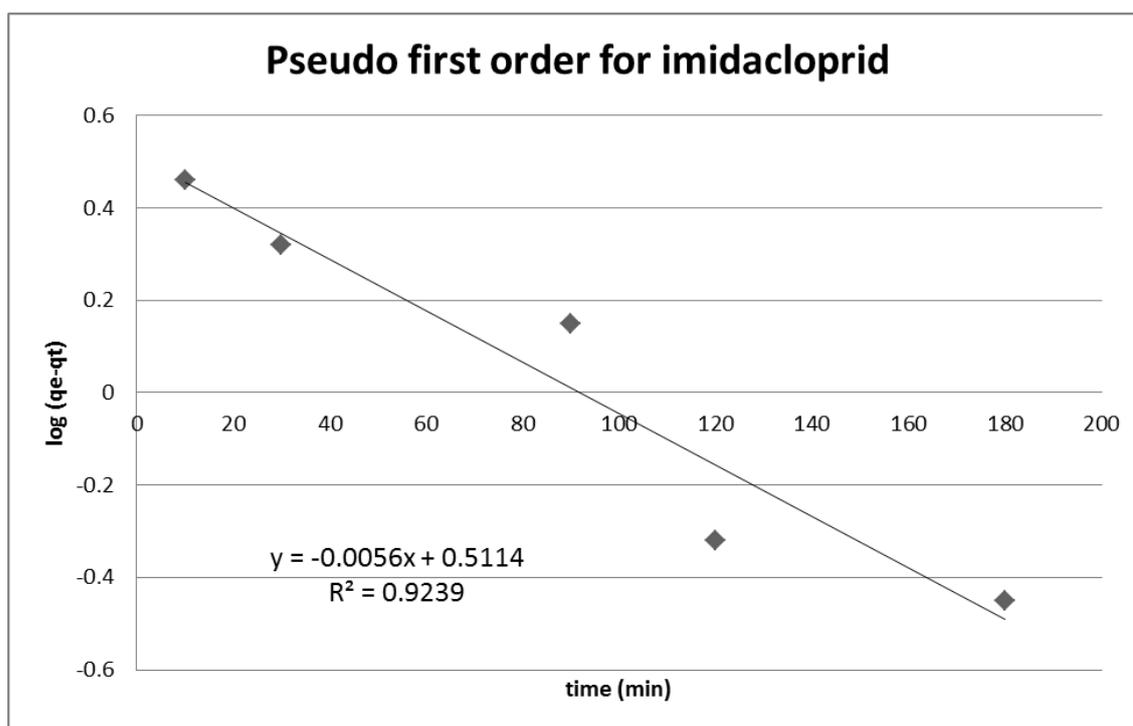
Figure 4.13 pseudo first order for imidacloprid.
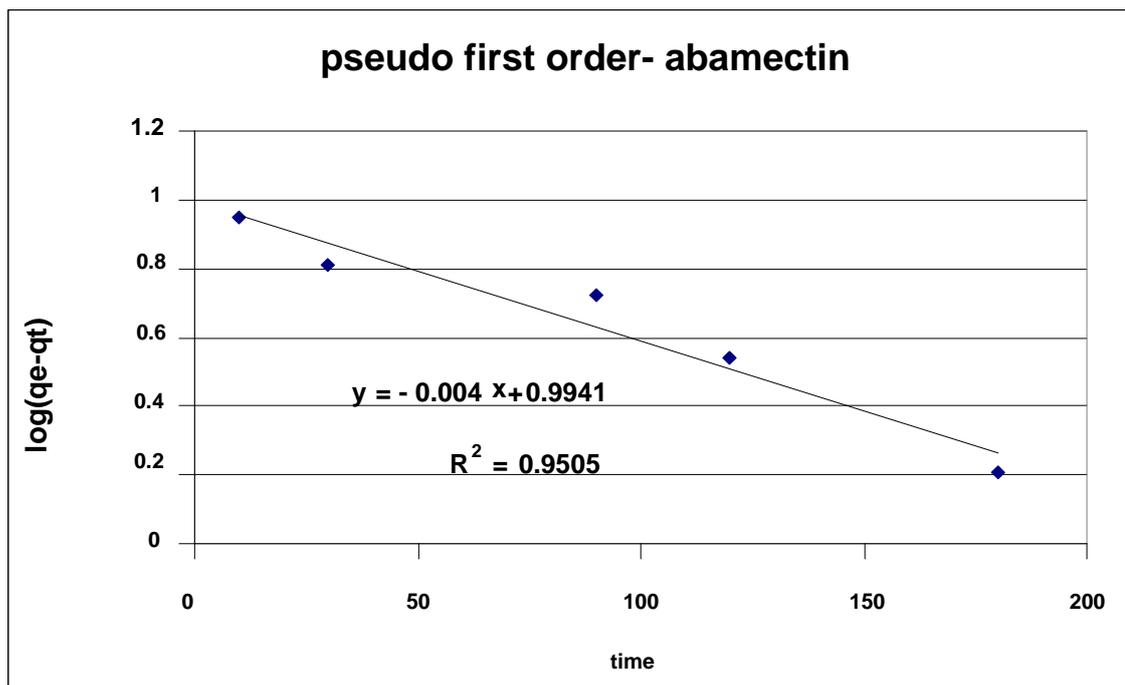
Figure 4.14 pseudo first order for abamectin.

4.11.2 Pseudo second order model

Second order rate constant was calculated by Equation (2).

$$t/qt = 1/k2*qe2 + t/qe \qquad (2)$$

plot of t/qt versus t had shown straight line with R^2 value 0.987 for imidacloprid and abamectin as shown in figure, from which it was concluded that kinetic adsorption of imidacloprid and abamectin had closely correlated with pseudo second order model,(**Fernandez-Bayo, *et al, 2008*). In chemisorption process, the pseudo second order is superior to pseudo-first order model because it deals with interaction of adsorbent-adsorbate through their valency forces,(**Bajeer, *et al*, 2012**).

Pseudo second order for imidacloprid

$y = 0.1944x + 17.525$

$R^2 = 0.9869$
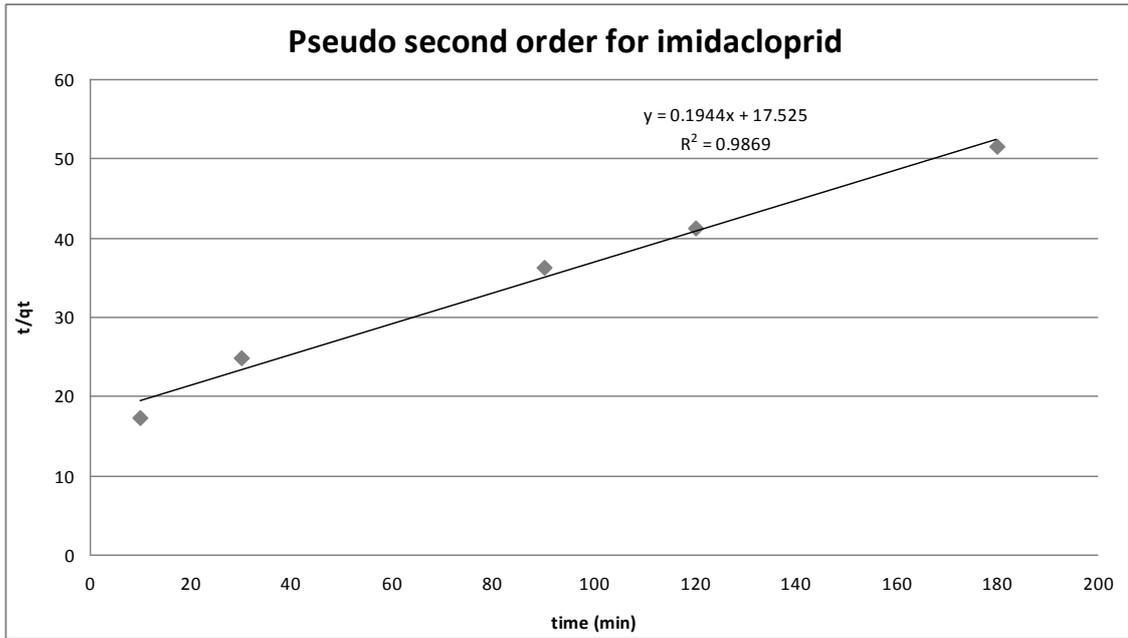
Figure 4.15 pseudo second order for imidacloprid.

Pseudo second order for abamectin

$y = 0.1571x + 8.8236$

$R^2 = 0.986$
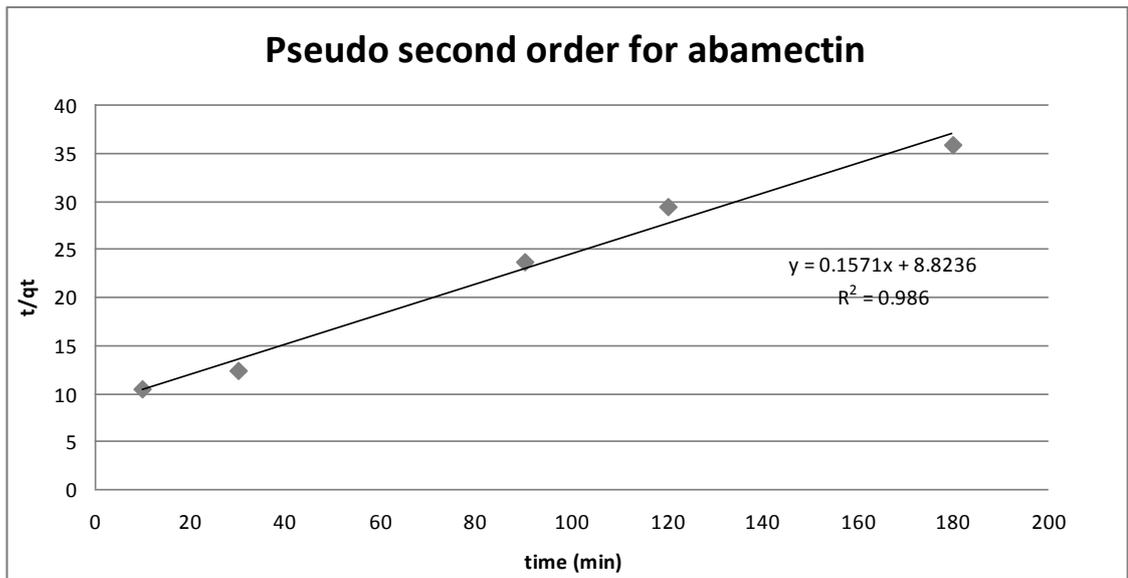
Figure 4.16 pseudo second order for abamectin.

The correlation coefficients and other parameters calculated for the Pseudo
-first-order model and pseudo-second-order model are listed in Table 4.4.
From Table 4.4, it is clear that the correlation coefficient values (R^2) of the

pseudo-second order model for imidacloprid and abamectin greater than those obtained for the pseudo-first order model.

Table 4.6: Pseudo-first-order and pseudo-second-order kinetic model parameters for imidacloprid and abamectin adsorption onto soil at 25 ºC

	Pseudo- first order			Pseudo - second order		
Adsorbate	Parameters			Parameters		
	K_1 (min-1)	q_e (calc)	R^2	K_2 (g/mg min)	q_e (calc)	R^2
Abamectin	0.0092	9.8651	0.9505	0.0039	5.3654	0.986
Imidacloprid	0.0129	3.2464	0.9239	0.0022	5.144	0.9869

4.11.3 Intra-particle diffusion kinetic model

The values of the intra-particle diffusion constants and the correlation Coefficients for imidacloprid and abamectin obtained from the linear plots of qt versus t ½, given in Figure 4.17 and 4.18, are summarized in Table 4.5.
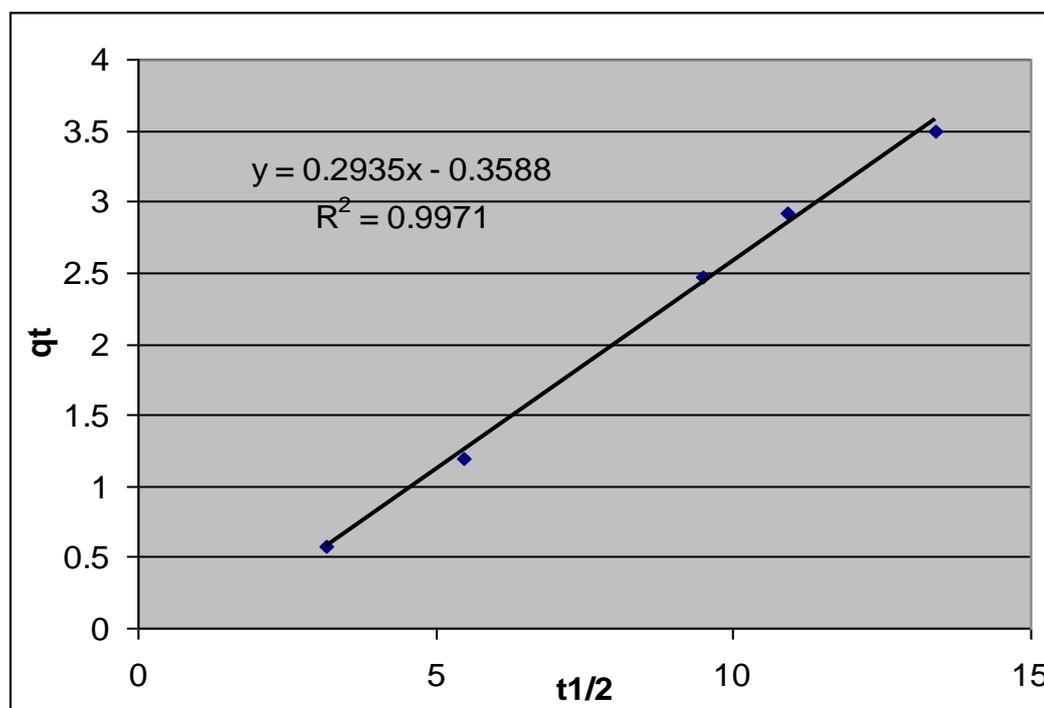
Figure 4.17: Kinetics of imidacloprid to the intra-particle diffusion model by soil at (initial conc: 50 mg/L, initial pH: 4, temperature: 25 ºC .
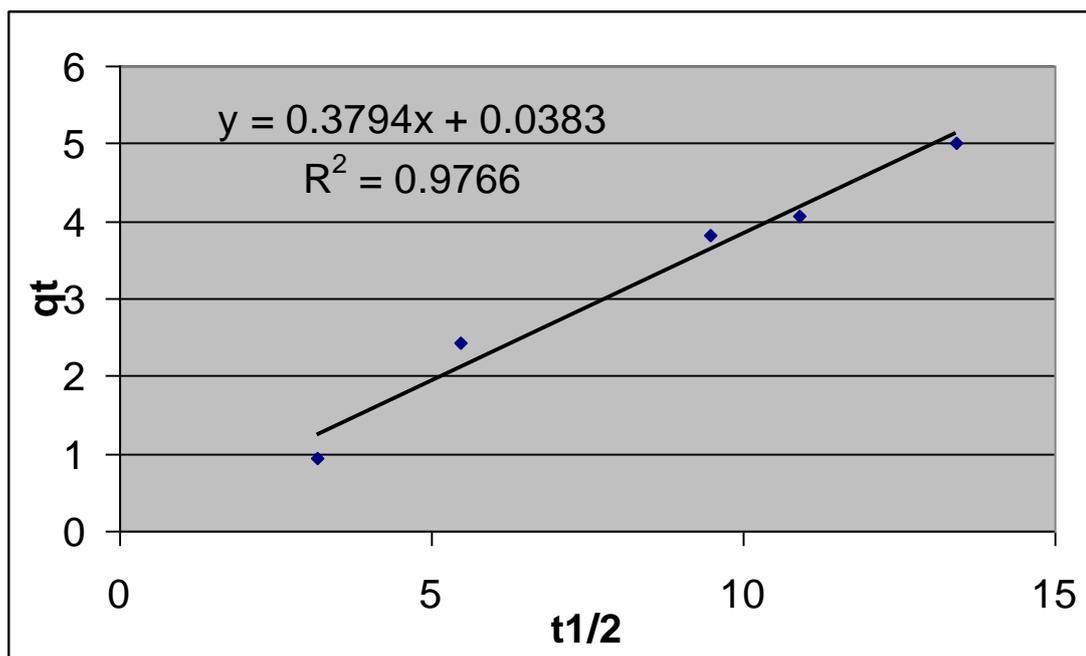
Figure 4.18: Kinetics of abamectin to the intra-particle diffusion model by soil at (initial conc: 50 mg/L, initial pH: 4, temperature: 25 ºC .

Table 4.7: Intra-particle diffusion kinetic model parameters for imidacloprid and abamectin adsorption onto soil at 25 ºC.

Adsorbent	K_p(mg/g min$^{1/2}$)	A	R^2
Abamectin	0.3787	0.041	0.9762
Imidacloprid	0.293	-0.358	0.9975

For the intra-particle diffusion the straight line in figure 4.17 did not pass through the origin, this indicates that the rate of imidacloprid adsorption onto soil is limited by mass transfer across the boundary layer, while in figure 4.18 for abamectin the straight line pass through the origin this implies that abamectin adsorption onto soil is not limited by mass transfer across the boundary layer.

4.12 Equilibrium Adsorption Study

4.12.1 Langmuir Isotherm Model

This model deals with monolayer and homogeneous adsorption because the adsorbed layer is one molecule in thickness, with adsorption occurring at fixed sites, which are identical and equivalent. Linear form of this model is given in Equation (3).

$$C_e/q_e = 1/Q_0*b + C_e/Q_0 \quad (3)$$

Where C_e is the equilibrium concentration of imidacloprid and abamectin in solution and q_e is the amount of imidacloprid and abamectin in soil surface, Q_0 is the monolayer adsorption capacity, and b is Langmuir isotherm which was not obeyed by adsorption of imidacloprid and abamectin.

Table 4.8 : The application of Langmuir isotherm for the adsorption of imidacloprid on soil.

qe	Ce	Ce\qe
94	48.12	0.512
190	46.2	0.243
290	44.2	0.152
367.5	42.65	0.116
460.5	40.79	0.089
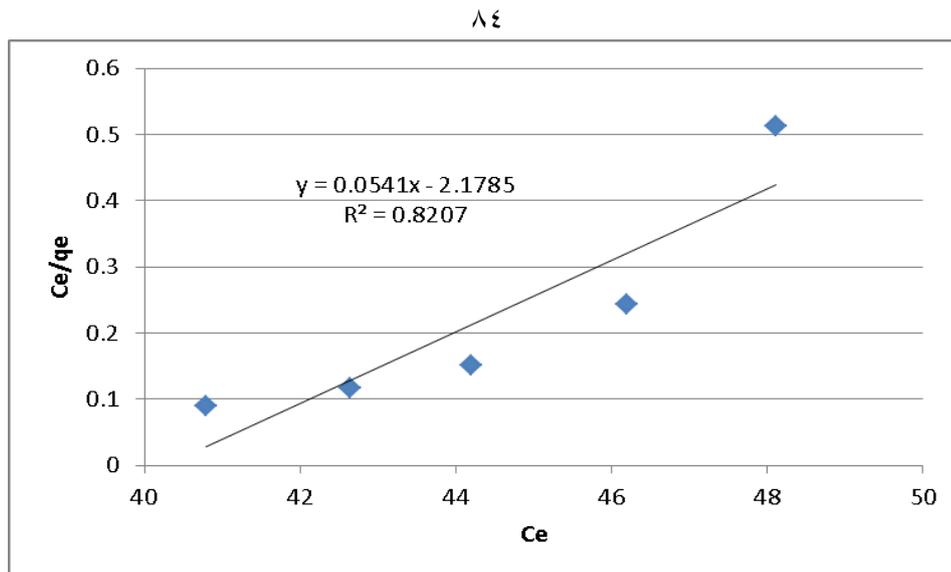
Figure 4.19 Langmuir isotherm for the adsorption of imidacloprid.

Table 4.9 : The application of Langmuir isotherm for the adsorption of abamectin on soil.

qe	Ce	Ce\qe
44.5	49.11	1.104
96.5	48.07	0.498
234	45.32	0.194
281	44.38	0.158
441.5	41.17	0.093
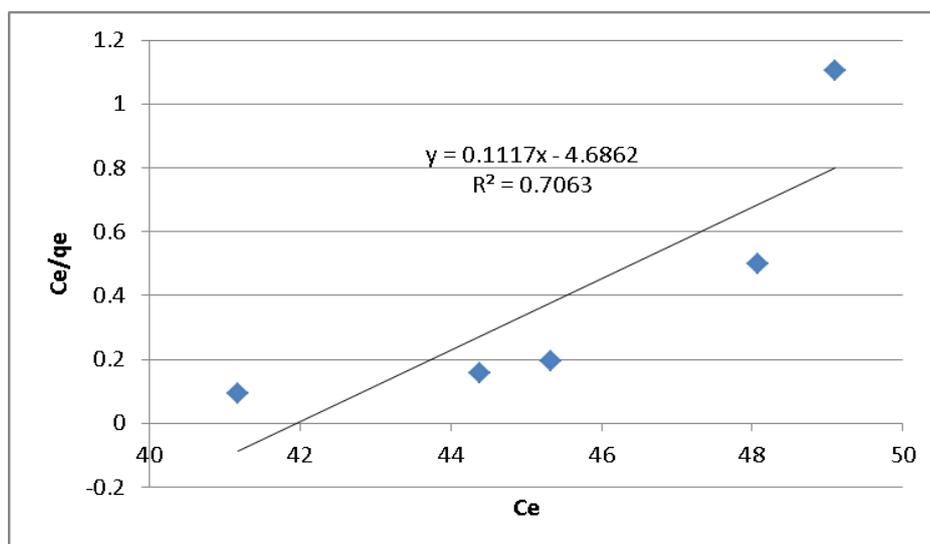
Figure 4.20 Langmuir isotherm for the adsorption of abamectin.

4.12.2 Freundlich Isotherm Model

Freundlich isotherm is related to the non-ideal and reversible adsorption, not limited to monolayer formation. Therefore is applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Linear form of this model is given as in Equation (4).

$$\text{Log } q_e = \log K_f + (1/n) \log C_e \qquad (4)$$

Where K_f is multilayer adsorption capacity and n is adsorption intensity. A plot of log q_e against log C_e gives straight line showing that this model was obeyed by adsorption of imidacloprid and abamectin. The parameters of both models are shown in table 4.10 .

The n values were 0.1067 and 0.0798 for imidacloprid and abamectin respectively showing that adsorption process was not favorable because n less than 1, and when n more than 1 and less than 10 represents the favorability of adsorption.

Table (4.10): The application of Freundlich isotherm for the adsorption of imidacloprid on soil .

qe	Ce	Log qe	Log Ce
94	48.12	1.973	1.682
190	46.2	2.279	1.665
290	44.2	2.462	1.645
367.5	42.65	2.565	1.629
460.5	40.79	2.663	1.611
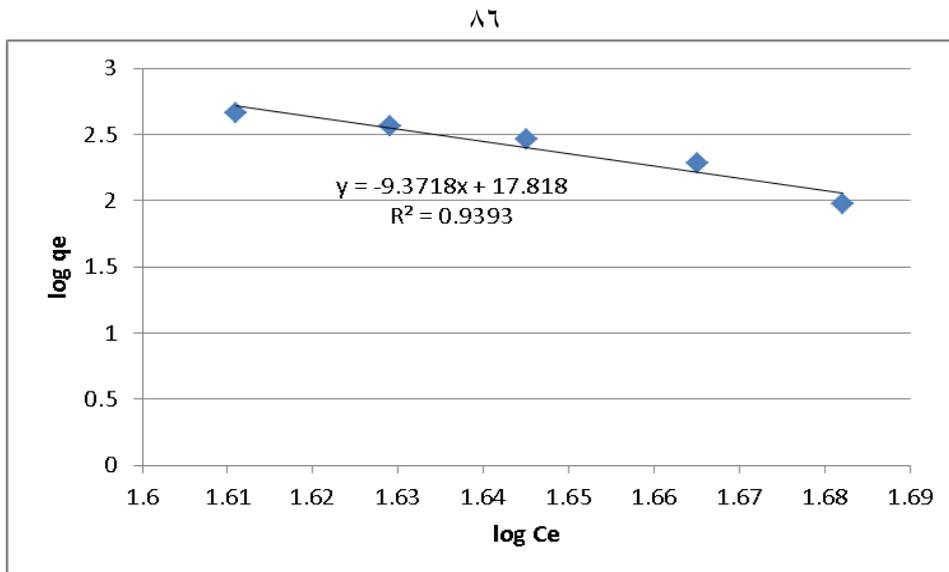
Figure 4.21 Freundlich isotherm for the adsorption of imidacloprid.

Table(4.11): The application of Freundlich isotherm for the adsorption of abamectin on soil .

qe	Ce	Log qe	Log Ce
44.5	49.11	1.648	1.691
96.5	48.07	1.985	1.682
234	45.32	2.369	1.656
281	44.38	2.449	1.647
441.5	41.17	2.645	1.615
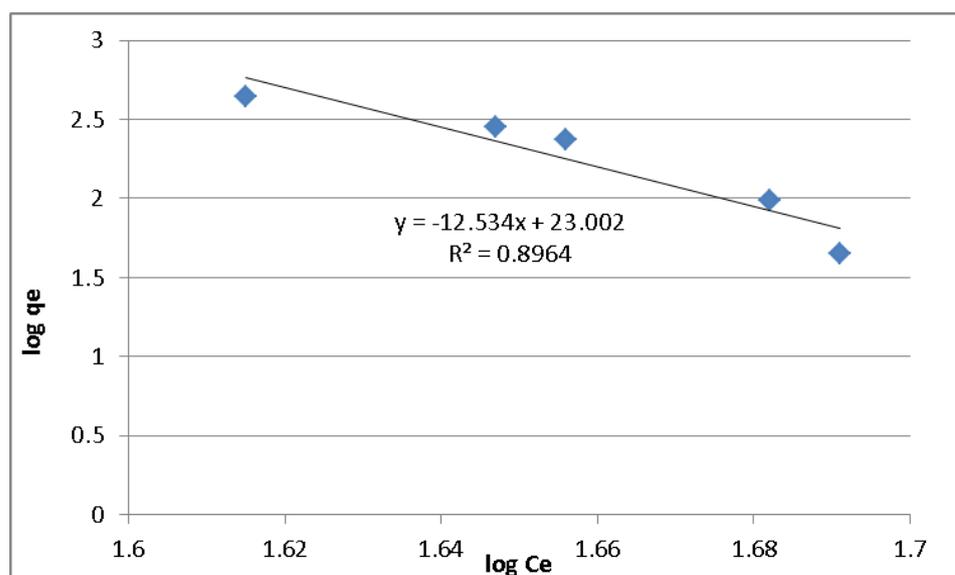
Figure 4.22 Freundlich isotherm for the adsorption of abamectin.

The Langmuir adsorption isotherm is commonly applied to monolayer chemisorptions of gases. This isotherm is mainly applied when no strong adsorption is expected and when the adsorption surface is uniform.

Table. 4.12 Langmuir and Freundlich isotherm model parameters and correlation coefficient of pesticides adsorption.

Isotherm	Langmuir Parameters			Freundlich Parameters		
Adsorbate	q_0 (mg/g)	b (L/mg)	R^2	K_f ((mg/g) $(L/mg)^{1/n}$)	n	R^2
Abamectin	9.953	0.0214	0.7063	1.0046×10^{23}	0.0798	0.8964
Imidacloprid	18.484	0.0248	0.8207	6.5766×10^{17}	0.1067	0.9393

Both the Langmuir and Freundlich adsorption isotherms showed linear relationship on the present results shown in figures (4.19), (4.20),(4.21), (4.22) for the Langmuir and Freundlich adsorption isotherms, respectively but R^2 for the Freundlich adsorption isotherms is larger than that in Langmuir adsorption isotherms and close to 1, so the application of the Freundlich adsorption isotherms was more appropriate, n values for the two pesticides were lower than "1" which indicate that the adsorption capacity and intensity respectively were low, and it leaves the soil quickly,(**Bajeer,** *et al***, 2012).**

Conclusion and Recommendation

Conclusions

Adsorption of imidacloprid and abamectin was studied and the following results were obtained:

1. Imidacloprid and abamectin soil adsorption in this study was increased with increasing temperature versus time.

2. The highest percentage of imidacloprid removal was 13.4 % when adsorbent dosage 3 g .

3. The highest percentage of abamectin removal was 7.5 % when adsorbent dosage 3 g.

4. Percentage removal of imidacloprid and abamectin increases when the concentration decreases.

5. At low pH "1.5" the percent of imidacloprid removal increases, but the decrease of imidacloprid removal at pH from 7 to 12 is highly extreme.

6. At high pH "12" the percent of abamectin removal increases, but the decrease of abamectin removal of pH from 7 to 9.

7. The results showed that equilibrium time for imidacloprid and abamectin adsorption is 150 min, but most the adsorption attained within the first 15 min.

8. The kinetic adsorption of imidacloprid and abamectin on soil followed pseudo second order.

9. The equilibrium adsorption of imidacloprid and abamectin on soil followed Freundlich isotherm.

10. The values of the intra-particle diffusion constants and the correlation coefficients implies that the rate of imidacloprid adsorption onto soil is limited by mass transfer across the boundary layer, while abamectin adsorption onto soil is not limited by mass transfer across the boundary layer.

Recommendations

To reduce pesticides environmental pollution, it is recommended to :

1. Using multiple methods of agricultural pest control, such as the physical and biological control and finally rely on chemical control to minimize pesticides pollution.

2. Disseminate awareness among farmers of the importance of the use of the recommended amounts of pesticides and non-use of high concentrations and comply with the instructions of use.

3. Concerned ministries should agree on a clear specification of responsibilities towards pesticides waste management in Palestine.

4. More laws and regulations related to pesticides waste management outside farms and away from the reach of children should be applied.

5. More researches in this regard should be carried out, further investigation into the fate and mobility of imidacloprid and abamectin in the environment.

6. Further improvement and validation of the employed methods for the analysis these pesticides in soil and water.

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Appendix

بسم الله الرحمن الرحيم

يهدف هذا الاستبيان المسحي إلى التعرف على أنواع المبيدات الزراعية المستخدمة من قبل المزارعين وكذلك معرفة الكميات التي يستخدمها المزارعين من هذه المبيدات،

نرجو من إخواننا المزارعين تعبئة الاستبيان بكل وضوح ومصداقية.

مع الشكر الجزيل،،،،،

الباحث: أسامة محمد خلف

يتكون الاستبيان من قسمين:

1) المعلومات العامة

2) المكافحة المستخدمة (الرش)

القسم الأول: المعلومات العامة
ضع دائرة حول الإجابة المناسبة
١) نوع الزراعة :

أـ مكشوف
بـ بيت بلاستيكي
تـ أنفاق بلاستيكية
٢) نوع السماد المستخدم :

أ) عضوي بلدي (زبل)

ب) كيميائي (اكياس)

ت) خليط بين النوعين السابقين

٣) نوعية المكافحة (الرش) :

أ)بيولوجية (كائنات حية)

ب) كيميائية (مبيدات)

ت) خليط بين النوعين السابقين

٤) نوعية المياه المستخدمة في الري :

أ)مياه جوفية (آبار)

ب) سطحية (برك)

ت) مياه مجاري مكررة

٥) نوعية البيت :

أ)ملك

ب) أجرة

ت) غير ذلك

٦) مدة العمل بالزراعة بالسنوات:

أ) ١ إلى ٣

ب) ٤ إلى ١٠

ت) فوق ١٠

القسم الثاني : المكافحة
ضع دائرة حول الإجابة المناسبة
١) أكثر المبيدات الحشرية استخداماً:

أ) كونفيدور

ب) دروسبان

ت) مارشال

٢) أكثر مبيدات العناكب استخداماً :

أ) نيرون

ب)فيرتميك

ت)مساي

٣) عدد رشات المبيدات الحشرية خلال الموسم :

أ) مرتين

ب) ٤ مرات

ت) فوق ٤ مرات

٤) عدد رشات مبيدات العناكب خلال الموسم :

أ) مرتين

ب) ٤ مرات

ت) فوق ٤ مرات

٥) يتم قراءة التعليمات على علبة المبيد :

أ) نعم

ب) لا

ت) غير ذلك

٦) يتم الالتزام بالكمية الموصى بها من قبل الشركة المصنعة (التركيز على علبة المبيد)

أ) نعم

ب) لا

ت) غير ذلك

٧) يلبس المزارع الكمامات أثناء تحضير المبيد :

أ) نعم

ب) لا

ت) غير ذلك

٨) يلبس المزارع القفازات أثناء فترة الرش :

أ) نعم

ب) لا

ت) غير ذلك

٩) يلبس نظارات الحماية أثناء فترة الرش :

أ) نعم

ب) لا

ت) غير ذلك

١٠) هل يتم إضافة السماد بـ :
أ)   جرة السماد من خلال شبكة الري

ب) رش السماد على أوراق النباتات

ت) إضافة السماد مباشرة على النباتات

جامعة النجاح الوطنية

كلية الدراسات العليا

حركة ومصير الكنفدور والفيرتميك ومتبقياتها في التربة

إعداد

أسامة محمد أحمد خلف

إشراف

أ . د. مروان حداد

د. شحدة جودة

قدمت هذه الأطروحة استكمالا لمتطلبات نيل درجة الماجستير في العلوم البيئية بكلية الدراسات العليا في جامع النجاح الوطنية في نابلس، فلسطين.

2013

ب

حركة ومصير الكنفدور والفيرتميك ومتبقياتها في التربة

إعداد

أسامة محمد أحمد خلف

إشراف

أ . د. مروان حداد

د. شحدة جودة

الملخص

أثار اهتمام المجتمع في الآونة الأخيرة وجود متبقيات المبيدات في التربة والمياه لما لها من تأثير على البيئة والنظام البيئي بشكل عام، ليمتد تأثيرها ويصل إلى الحيوانات والإنسان.

في هذه الدراسة تم اختيار نوعين من المبيدات وهما الاميداكلوبريد (كونفدور) كمثال على المبيدات الحشرية والابمكتين (فيرتميك) كمثال على مبيدات العناكب. وهما الأكثر استخداما في فلسطين اعتمادا على نتائج الاستبيان الذي اجري.

في هذا البحث تم دراسة السلوك الامتصاصي لهذه المبيدات في التربة، والعديد من العوامل التي قد تؤثر في عملية الامتصاص مثل درجة الحرارة ودرجة الحموضة والجرعة الممتصة ووقت التماس والتركيز حيث تمت جميع هذه الدراسات باستخدام جهاز الامتصاص الطيفي للأشعة فوق البنفسجية والضوء المرئي UV-Vis spectrophotometer.

وقد أشارت النتائج إلى أن أعلى نسبة استخلاص للاميداكلوبريد والابمكتين كانت 13.4 % و 7.5% على التوالي عندما كانت كمية التربة المستخدمة (3غم). نسبة استخلاص الاميداكلوبريد والابمكتين تزداد كلما قل التركيز، أعلى نسبة استخلاص وصلت 17% للاميداكلوبريد و 19% للابمكتين عندما كان تركيزهم 10ملغم/لتر و 1غم تربة. عندما يكون الرقم الهيدروجيني منخفض "1.5" نسبة استخلاص الاميداكلوبريد تزداد وتصل إلى12.3 %، لكن نقصان استخلاص الاميداكلوبريد عند الرقم الهيدروجيني "12" يصل فقط إلى 7.3%. نسبة استخلاص الابمكتين عند الرقم الهيدروجيني "12" تزداد وتصل إلى 15.4%، لكن اقل نسبة استخلاص للابمكتين عند الرقم الهيدروجيني "7" وتصل إلى 9.1%. اثر درجة الحرارة على الادمصاص بوساطة التربة تم التحقق

منــه فــي نطــاق مــن 15-47 درجــة مئويــة. تشــير النتــائج فــي هــذه الدراســة إلــى أن امتصــاص الاميداكلوبريد والابمكتين في التربة يزداد مع ازدياد درجة الحرارة. ولقد أظهرت النتائج إلى أن زمن الاتزان لعملية الادمصاص هو 150 دقيقة ولكن معظم هذه العملية تمت بالدقائق الخمس عشرة الأولى.

تهدف هذه الدراسة لتقييم الادمصاص وإمكانية الرشح وحركة ومصير الاميداكلوبريد والابمكتين في التربة. لفهم آلية الادمصاص والعوامل المؤثرة، أجريت التجارب في ظل ظروف المختبر. دراسة الادمصاص قسمت إلى حركية وتوازنية. وقد تم تقييم البيانات الحركية من خلال نموذج الاعتماد من الدرجـة الأولـى ظاهريا ونموذج الاعتماد من الدرجة الثانية ظاهريا ونموذج تدفق الدقائق إلى داخل الجسيمات. وقد وجد أن الادمصاص الحركي للإميداكلوبريد والأبمكتين في التربة يتبع نموذج الاعتمــاد مــن الدرجــة الثانيــة ظاهريــا. تــم اســتخدام معــادلتي (لانجميــر) و (فريندليش) لتوضــيح الادمصاص عند الاتزان، حيث كان نموذج (فريندليش) انسب لتفسير الادمصاص لدى المبيدان على التربة.