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Adsorption and Leaching Potential of Pesticides on Soil Samples in Jordan

M.Sc. Thesis By

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A Thesis Submitted in Partial Fulfillment of the Requirements for
the Degree of Master in Civil Engineering

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Muscat
Sultanate of Oman

April, 2018

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Adsorption and leaching potential of
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**ADSORPTION AND LEACHING POTENTIAL OF PESTICIDES ON
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**This Thesis was submitted in Partial Fulfillment of the Requierments for the
Master's Degree in Civil Engineering**

**School of Graduate Studies
The University of Jordan**

April, 2018



COMMITTEE DECISION

This thesis (Adsorption and Leaching Potential of Pesticides on Soil Samples in Jordan) was Successfully Defended and Approved on 24/4/2018

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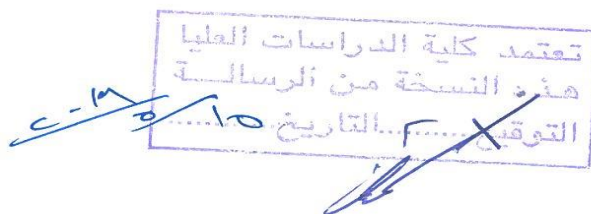
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DEDICATION

I dedicate this thesis to my family for their endless love, encouragement and support.

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LIST OF ABBREVIATIONS OR SYMBOLS

Ce	Equilibrium concentration of adsorbate in solution after adsorption
DDT	Dichlorodiphenyltrichloroethane
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
GC-MS	Gas Chromatography-Mass spectrometry
K₁	The rate constant of the pseudo-first order model
K₂	The rate constant of the pseudo-first order model
K_f	Freundlich capacity factor
K_L	Langmuir's constant
MgSO₄	Magnesium Sulfate
N	Freundlich intensity parameter
NaCl	Sodium Chloride
ppm	Part per million
Q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium
Q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at any time
Q_m	Maximum adsorption capacity of the adsorbent
Rpm	Rounds per minute
SOM	Soil Organic Matter
TOM	Total Organic Matter
WHO	World Health Organization

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ADSORPTION AND LEACHING POTENTIAL OF PESTICIDES IN SOIL SAMPLES IN JORDAN

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ABSTRACT

In this thesis adsorption behavior of cypermethrin and chlorfenapyr is studied using batch method. Soil samples from two locations with depth of (0-30) cm in Tafilah-Jordan were selected and analyzed. Primary investigations to determine the soil characteristics were conducted. The results indicated that the texture of the two samples were sandy. The content of organic matter was 1.77% for soil (1) and 2.02% for soil (2).

Adsorption study is divided into: kinetic and equilibrium sections. The evaluation of kinetic data is done through pseudo first and second order models. It was found that kinetic adsorption of cypermethrin and chlorfenapyr on soil samples followed pseudo second order with rate constant values of (1.009 g/mg.hr: cypermethrin, 11.379 g/mg.hr: chlorfenapyr) for soil (1) and (2.032 g/mg.hr: cypermethrin, 13.032 g/mg.hr: chlorfenapyr) for soil (2).

Langmuir and Freundlich isotherms were used to explain equilibrium adsorption, from these isotherms it was found that Langmuir isotherm applied well with maximum adsorption capacities of (9.083 mg/g: cypermethrin, 36.2318 mg/g: chlorfenapyr) for soil (1) and (8.881 mg/g: cypermethrin, 45.2488 mg/g: chlorfenapyr) for soil (2).

The soil adsorption coefficient ($\text{Log } K_{oc}$) values for cypermethrin and chlorfenapyr are between (3.5-4.5) which indicates for strong adsorption to soil and negligible to slow leaching to groundwater. So, the potential leaching of cypermethrin and chlorfenapyr to groundwater is very low; because of good soil samples and the physical properties of pesticides.

CHAPTER 1

INTRODUCTION

The utilization and production of pesticides are increasing worldwide day by day. It is important to know that when pesticides are applied to the field, only small portion reaches to its target and the remaining large part is released into the environment. That may lead to some problems, such as toxicity to non-target organisms, leaching to groundwater and accumulation in the soil. Polluted soil, surface and ground waters involve risk to the environment and to human health due to possible direct or indirect exposures (Bajeer et al., 2012).

1.1 Significance and Objectives of This Study

Cypermethrin is a synthetic pyrethroid used as an insecticide in large-scale commercial agricultural applications. Chlorfenapyr is a pesticide, and specifically a pro-insecticide, derived from a class of microbial produced compounds known as halogenated pyrroles. They are used in Jordan in large quantities. There are many human health effects of cypermethrin and chlorfenapyr and there is risk if its finding its way into human food chains by accumulation in soil and water resources. Thus, it is important to investigate the fate and behavior of these pesticides in soil environment. Adsorption of cypermethrin and chlorfenapyr onto soil organo-mineral solid phases is the main process that controls its transportation and transformation processes.

The objectives of this study are:

The objectives of this work were to determine adsorption behavior of cypermethrin and chlorfenapyr in the typical agricultural soils of Tafilah, Jordan. Kinetics and isotherm adsorption experiments were carried out to have a better insight into the adsorption process. The specific objectives of this study are:

- 1- To determine the portion of the cypermethrin and chlorfenapyr that leach to groundwater.
- 2- To study the adsorption of cypermethrin and chlorfenapyr on soil samples.

1.2 Thesis Organization

A literature review related to this study is presented in chapter two which reviews the adsorption of cypermethrin and chlorfenapyr onto soil and the factors that may affect the adsorption process.

Chapter three states materials and methods used in this work. Results of kinetic and equilibrium adsorption studies of cypermethrin and chlorfenapyr onto soils are discussed in Chapter four, And the conclusion and recommendations of this study are discussed in chapter five.

CHAPTER 2

LITERATURE REVIEW

2.1 Pesticides History and Classification

According to Food and Agriculture Organization (1989), a pesticide is any substance or mixture of substances intended for preventing, destroying, or controlling any pest including vectors of human or animal diseases, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, or marketing of food, agricultural commodities, wood and wood products, or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies.

The term includes chemicals used as a plant growth regulator, defoliants, desiccants, fruit thinning agents, or agents for preventing the premature fall of fruits, and substances applied to crops either before or after harvest to prevent deterioration during storage or transport (FAO, 1989).

Since before 500 BC, humans have used pesticides to prevent damage to their crops. The first known pesticide was sulfur. By the 15th century, toxic chemicals such as arsenic, mercury and lead were being applied to crops to kill pests. In the 17th century, nicotine sulfate was extracted from tobacco leaves for use as an insecticide. The 19th century saw the introduction of two more natural pesticides, pyrethrum which is derived from chrysanthemums, and rotenone which is derived from the roots of tropical vegetables (Miller, 2002).

In 1939, Paul Müller discovered that DDT was a very effective insecticide. It quickly became the most widely-used pesticide in the world (Miller, 2002).

However, in the 1960s, it was discovered that DDT was preventing many fish-eating birds from reproducing which was a huge threat to biodiversity. Rachel Carson wrote the best-selling book “Silent Spring” about biological magnification. DDT is now banned in at least 86 countries, but it is still used in some developing nations to prevent malaria and other tropical diseases by killing mosquitos and other disease-carrying insects. Pesticide use has increased 50-fold since 1950, and 2.5 million tons of industrial pesticides are now used each year (Lobe, 2006).

The word “pesticide” is an umbrella term for all insecticides, fungicides, herbicides, rodenticides, garden chemicals, wood preservatives, and household disinfectants that may be used to kill some pests. Pesticides have different identities and physical and chemical properties. Synthetic pesticides are classified based on various ways. In general, there are three main ways to classify them: classification based on the (i) mode of action, (ii) targeted pest species, and (iii) chemical composition of pesticides (Drum, 1980).

In the last type of classification, pesticides are characterized regarding their chemical nature and active ingredients. This is the most useful one for researchers studying the field of pesticides and the environment, because this kind of classification gives the clue of the efficacy and physical and chemical properties of the respective pesticides and precautions that need to be taken during application and the application rates, the knowledge of which is important in the mode of application (Tano, 2011).

According to chemical properties, pesticides can be generally divided into about seven types, including organochlorines, organophosphorus, carbamates, pyrethroids, amides, anilins, and azotic heterocyclic compounds (Zhang Y, 2007).

Except for these classifications, pesticides are classified according to the mode of formulation, activity spectrum, and toxicity level. According to the mode of formulation, pesticides are classified into six groups as wettable powders, emulsifiable concentrates, baits, granules, dusts, and fumigants. In active spectrum, pesticides are classified into two groups as broad-spectrum pesticides and selective pesticides. Broad-spectrum pesticides are designed to kill a wide range of pests and other nontarget organisms. On the contrary, selective pesticides are designed to kill only specific pests. In toxicity level, the World Health Organization (WHO) has developed a classification system that group pesticides according to the potential risks to human health and they are grouped into the following classes: class Ia=extremely hazardous, class Ib=highly hazardous, class II=moderately hazardous, class III=slightly hazardous, and class IV=products unlikely to present acute hazards in normal use (Tano, 2011).

2.2 Pesticides Effects on Soil

Many of the chemicals used in pesticides are persistent soil contaminants, whose impact may endure for decades and adversely affect soil conservation (USEPA, 2007).

The use of pesticides decreases the general biodiversity in the soil. Not using the chemicals results in higher soil quality (Johnston, A.E. 1986), with the additional effect that more organic matter in the soil allows for higher water retention (Kellogg, et al., 2000). This helps

increase yields for farms in drought years, when organic farms have had yields 20-40% higher than their conventional counterparts (Lotter, D. et al., 2003) a smaller content of organic matter in the soil increases the amount of pesticide that will leave the area of application, because organic matter binds to and helps break down pesticides (Kellogg, et al., 2000).

The capacity of the soil to filter, buffer, degrade, immobilize, and detoxify pesticides is a function of quality of the soil (Cameron, et. al., 1996). Soil quality also encompasses the impacts that soil management can have on water and air quality, and on human and animal health (Stolze et. al., 2000). The presence and bio-availability of pesticides in soil can adversely impact human and animal health, and beneficial plants and soil organisms. Pesticides move off-site contaminating surface and ground water and possibly causing adverse impacts on aquatic ecosystems (Jaenicke, E.C., 1998).

Pesticides that reach the soil can alter the soil microbial diversity and microbial biomass. Any alteration in the activities of soil microorganisms due to applied pesticides eventually leads to the disturbance in soil ecosystem and loss of soil fertility (Handa et al., 1999).

Pesticides have also been reported to influence mineralization of soil organic matter, which is a key soil property that determines the soil quality and productivity (Sebiomo et al., 2011).

2.3 The fate of pesticides in the environment

Ideally, a pesticide stays in the treated area long enough to produce the desired effect and then degrades into harmless materials. Three primary modes of degradation occur in soils:

- biological - breakdown by micro-organisms

- chemical - breakdown by chemical reactions, such as hydrolysis and redox reactions
- photochemical - breakdown by ultraviolet or visible light

The rate at which a chemical degrades is expressed as the half-life, which is the amount of time it takes for half of the pesticide to be converted into something else, or until its concentration is half of its initial level. The half-life of a pesticide depends on soil type, its formulation, and environmental conditions such as temperature and moisture levels.

Other processes that influence the fate of the chemical include plant absorption, soil adhesion, leaching, and vaporization. If pesticides migrate from their targets due to wind drift, runoff or leaching, they are considered to be pollutants. The potential for pesticides to move depends on the chemical properties and formulation of the pesticide, soil properties, the rate and method of application, pesticide persistence, frequency and timing of rainfall, irrigation, and depth to ground water (Winter, 1992). These processes are summarized in Figure (2.1).

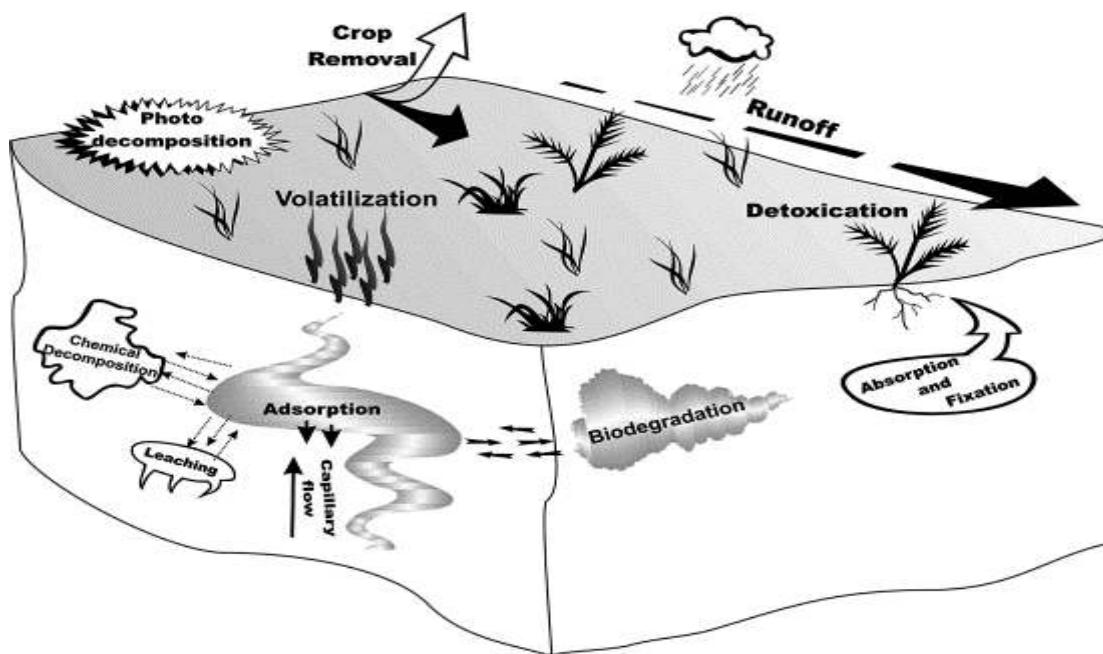


Figure (2.1): Fate of pesticides in soil (Strandberg et al., 1998).

2.4 Leaching to Groundwater

Leaching is the movement of pollutants through the soil by drainage water. The contamination of water bodies with pesticides can pose a significant threat to aquatic ecosystems and drinking water resources. Leaching of water and dissolved pesticides to groundwater occurs by matrix flow and preferential flow. Matrix flow is the slower transport process in which the simultaneous movement of pesticides with water is determined by soil structure, soil organic matter (SOM) and clay content and by physio-chemical properties of pesticide, including water solubility, vapor pressure and K_{oc} (Tiryaki and Temur 2010). Other factors affecting pesticides leaching are weather, application rate and season (Reichenberger et al., 2007). Preferential flow is the faster transport process depending on the presence of cracks and macropores, including biopores.

Leaching of pesticides occurs through mass transfer and molecular diffusion and is governed by mass flow and dispersion and is expected to be lower in soils high in SOM (Chesters et al., 1989). Except to diquat and paraquat (Helling 1970), SOM is more closely related to leaching than is clay, obviously due to SOM being the principal sorbent (Mueller and Banks 1991). Moreover, in fine-textured soils, macropores, which are principally root channels and wormholes, may contribute to the leaching of pesticides. Soil pH can also influence leaching indirectly by influencing sorption, as demonstrated for triazines and sulfonylurea herbicides (Rolf Nieder, 2018).

Studies on residue of various pesticides bound to SOM showed its significance for the accumulation, toxicity, and bioavailability of these bound residues, which greatly influence their leaching behavior (Scheuner and Reuter 2000). There are many studies involving

leaching experiments either at laboratory (e.g. Van Genuchten and Cleary 1979; Veeh et al., 1994) or field scale (Kookana et al., 1995; Flury 1996; Sarmah et al., 2000), which demonstrated that pesticides can move beyond the rooting zone. Understanding this process is therefore a prerequisite to quantify the groundwater contamination potential of a given pesticides.

2.5 Cypermethrin and Chlorfenapyr

2.5.1 Cypermethrin

Cypermethrin is a synthetic, pyrethroid insecticide that has high insecticidal activity, low avian and mammalian toxicity, and adequate stability in air and light (Kaufman et al., 1981, and U.S.D.A., 1995). It is used to control many pests including lepidopterous pests of cotton, fruit, and vegetable crops and is available as an emulsifiable concentrate or wettable powder.

2.5.1.1 Structure

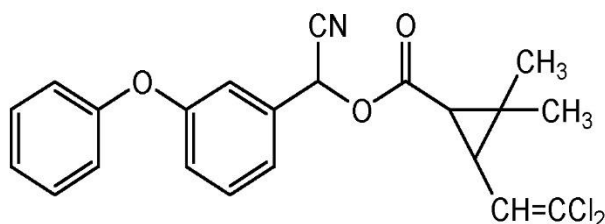


Figure (2.2): Structure of cypermethrin (USEPA, 1989)

IUPAC name: [cyano-(3-phenoxyphenyl) methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate

Chemical Formula: C₂₂H₁₉Cl₂NO₃

2.5.1.2 Toxicological Effects

Cypermethrin is a moderately toxic material by dermal absorption or ingestion (Meister et al., 1992 and Occupational Health Services, 1993). It may cause irritation to the skin and eyes. Symptoms of dermal exposure include numbness, tingling, itching, burning sensation, loss of bladder control, incoordination, seizures and possible death (Occupational Health Services, 1993). Pyrethroids may adversely affect the central nervous system (Occupational Health Services, 1993). Human volunteers given dermal doses of 130 ug/cm² on the earlobe experienced local tingling and burning sensations (Hayes et al., 1990).

One man died after eating a meal cooked in a 10% cypermethrin concentrate that was mistakenly used for cooking oil. Shortly after the meal, the victim experienced nausea, prolonged vomiting, stomach pains, and diarrhea which progressed to convulsions, unconsciousness and coma. Other family members exhibited milder symptoms and survived after hospital treatment (Hayes et al., 1990). Rats fed high doses of 37.5 mg/kg of the cis-isomer of cypermethrin for 5 weeks exhibited severe motor incoordination, while 20-30% of rats fed 85 mg/kg died 4 to 17 days after treatment began (Hayes et al., 1990). Cypermethrin is not a skin or eye irritant, but it may cause allergic skin reactions (U.S. Environmental Protection Agency, 1989).

Long-term exposure to cypermethrin may cause liver changes. Pathological changes in the cortex of the thymus, liver, adrenal glands, lungs and skin were observed in rabbits repeatedly fed cypermethrin (Occupational Health Services, 1993). EPA has classified cypermethrin as a weak possible human carcinogen because there is some evidence that it caused benign lung tumors in only one sex and one species (female mice) tested, and then only at the highest

dose tested (1,600 ppm). No tumors occurred in rats given doses of up to 75 mg/kg (U.S. Environmental Protection Agency, 1989).

2.5.2 Chlorfenapyr

Chlorfenapyr is a member of a new class of chemicals known as the pyrroles. The compound is a pro-insecticide, i.e. the biological activity depends on its activation to another chemical. Oxidative removal of the N-ethoxymethyl group of chlorfenapyr by mixed function oxidases forms the compound CL 303268. CL 303268 uncouples oxidative phosphorylation at the mitochondria, resulting in disruption of production of ATP, cellular death, and ultimately organism mortality (USEPA, 2001).

Chlorfenapyr has not been previously registered in the United States. However, it has been used for cotton (under the trade name Pirate) under Sec. 18 of the Federal Insecticide Fungicide and Rodenticide Act (FIFRA). The use on ornamental crops grown in greenhouses is a non-food use so there will be no dietary exposure. Since there are no residential uses of chlorfenapyr, no chronic residential exposure is anticipated (USEPA, 2001).

2.5.2.1 Structure:

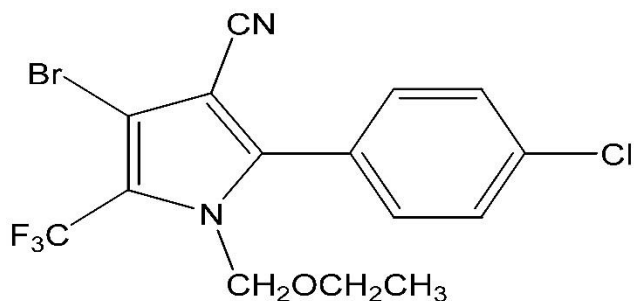


Figure (2.3): Structure of chlorfenapyr (USEPA, 2001)

IUPAC name: 4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)-1*H*-pyrrole-3-carbonitrile

Chemical Formula: C₁₅H₁₁BrClF₃N₂O

2.5.2.2 Toxicological Effects

Chlorfenapyr is harmful if swallowed. It causes eye irritation and it is toxic if inhaled. Chlorfenapyr may cause damage to organs through prolonged or repeated exposure. It is very toxic to aquatic life, with long-lasting effects (Krieger,2001).

Survivors of exposure to the metabolites exhibited no lasting clinical effects or notable findings during gross necropsy. There were no weight changes reported for survivors. Clinical signs reported for exposure to the metabolites included decreased activity, prostration, ptosis, increased salivation, and diuresis. Abnormalities noted at necropsy included discolored livers and spleens, discolored and distended stomachs, and gas-filled gastrointestinal tracts. Striated muscle tissue was reported in animals killed by AC 303,268 (Krieger,2001).

2.5.3 Physical properties

The physical properties of cypermethrin (Kollman and Segawa, 1995) and chlorfenapyr (USEPA, 2001) are given in Table (2.1).

Table (2.1): Physical properties of cypermethrin and chlorfenapyr

Property	Cypermethrin	Chlorfenapyr
Molar Mass	416.3 g/mol	407.6 g/mol
Density	1.24 g/ cm ³ at 20°C	0.4318 g/cm ³ at 20 °C
Melting Point	61-83°C	101.4 - 102.3°C
Solubility in Water	4 x 10 ⁻³ mg/L at 20°C	0.14 mg/L at 20°C
Vapor Pressure	1.3 x 10 ⁻⁹ mm Hg at 20°C	8.9 x 10 ⁻⁸ mm Hg at 20°C
Henry's law constant	2.5x10 ⁻⁷ atm-m ³ /mol	4.49 x 10 ⁻⁷ atm-m ³ /mol
Octanol/water partition coefficient K_{ow}	3.98 x 10 ⁶	1.91 × 10 ⁵

2.6 Adsorption

2.6.1 Adsorption process

Adsorption is one of the most important processes which controls all other processes such as their movement, persistence and degradation and determines the fate of pesticides in soil systems (Baer and Calvet, 1999).

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface (Glossary, 2009) . This process creates a film of the adsorbate on the surface of the adsorbent.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van

der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction (Ferrari et. al., 2010).

The adsorption process Figure (2.4) takes place in four, more or less definable steps: (1) bulk solution transport, (2) film diffusion transport, (3) pore and surface transport, and (4) adsorption (or sorption). The adsorption step involves the attachment of the material to be adsorbed to the adsorbent at an available adsorption sites (Snoeyink and Summers, 1999).

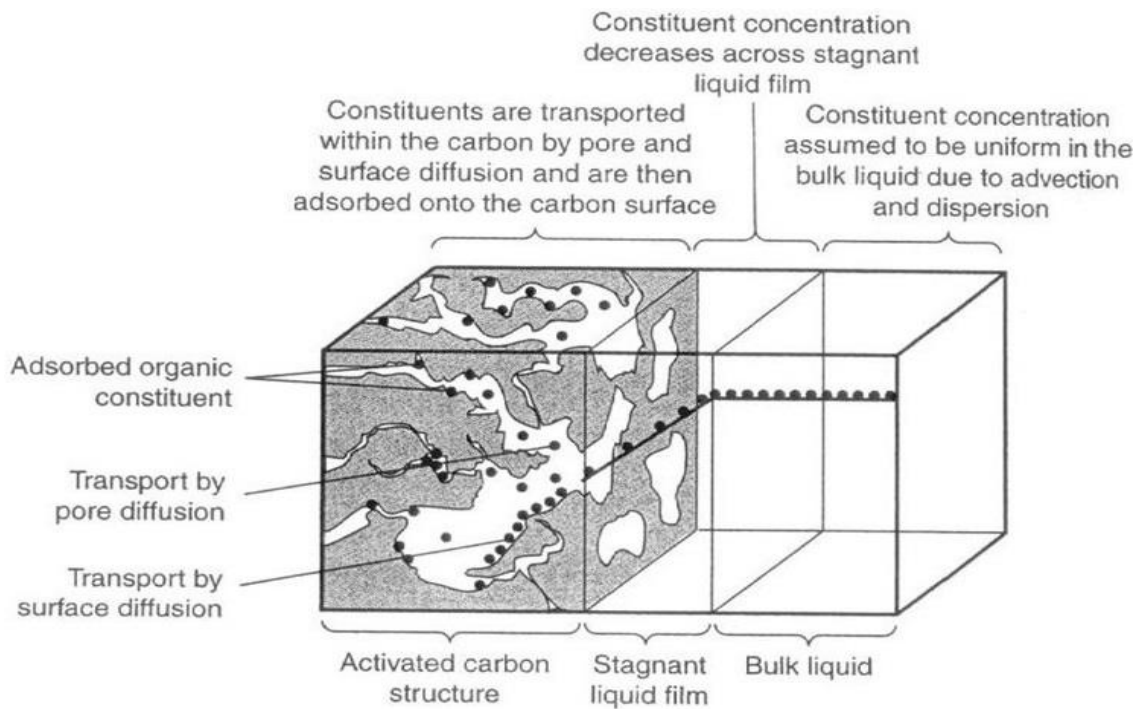


Figure (2.4): The adsorption steps (Snoeyink and Summers, 1999).

The amount of pesticides uptake (q_e) by soils was obtained as follows:

$$q_e = ([C_o - C_e]/m) * V \dots\dots\dots(2-1)$$

Where C_o and C_e are the initial and equilibrium concentrations of pesticides in solution (mg/L), respectively, V is the volume of the solution (L), and m is the mass of soil used (g).

Removal percentage of pesticides

The percentage removal of pesticides ($R_{em} \%$) in solution is calculated using equation:

$$R_{em} (\%) = ((C_o - C_e)/C_o) * 100 \dots\dots\dots(2-2)$$

2.6.2 Kinetics of adsorption

Several kinetics models have been applied to examine the controlling mechanism of pesticides adsorption from soil. In this study pseudo-first-order and pseudo-second-order is applied.

2.6.2.1 Pseudo-first-order reaction kinetics

The pseudo first order reaction model of Lagergren is a widely used for adsorption data analysis. This kinetic model is used for reversible reaction with an equilibrium being established between liquid and solid phase (Low et al., 2000) it is represented by (Ho and McKay, 1999):

$$dq_t/dt = k_1(q_e - q_t) \dots\dots\dots(2-3)$$

The linear form of the equation above is:

$$\text{Log}(q_e - q_t) = \text{log} q_e - (K_1/2.303) * t \dots\dots\dots(2-4)$$

Where q_t is the amount of pesticide adsorbed (mg/g) at any time t , q_e denotes the amount of pesticide adsorbed (mg/g) at equilibrium and k_1 (hr^{-1}) is the observed rate constant of pseudo-first-order kinetic model.

k_1 and q_e values will be obtained by plotting $\log (q_e - q_t)$ versus t .

2.6.2.2 Pseudo-second-order reaction kinetics

This model based on the assumption that the rate-limiting factor may be chemisorption (Low et al., 2000). In chemisorption (chemical adsorption), the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface (Kumar and Kirthika, 2009). In other words, chemisorption involves valence forces through sharing or exchange of electrons between the metal ions and the adsorbent. The rate law of this system is expressed as (Ho and McKay, 1999):

$$dq_t/dt = k_2(q_e - q_t)^2 \dots\dots\dots(2-5)$$

The linearized form of the pseudo-second-order model as given by Ho is:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e) * t \dots\dots\dots(2-6)$$

As mentioned before, q_t and q_e are the amounts of pesticide adsorbed (mg/g) at any time t and at equilibrium respectively, k_2 ($\text{g.mg}^{-1}.\text{hr}^{-1}$) is the rate constant of the pseudo-second-order model.

k_2 and q_e values will be obtained by plotting t/q_t versus t .

2.6.3 Adsorption Isotherms

The process of adsorption is usually studied through graphs known as adsorption isotherm. It is the graph between the amounts of adsorbate per unit mass of adsorbent and the

concentration of adsorbate remaining in solution at equilibrium at constant (isothermal) temperature (Kundu and Gupta, 2006). Different adsorption isotherms have been used are Freundlich, Langmuir and BET theory.

2.6.3.1 Freundlich Isotherm

Freundlich equation is an empirical equation employed heterogeneous system (Hammed et al., 2007); The Freundlich adsorption isotherm is experimentally derived and empirical.

According to The Freundlich equation, the logarithm of adsorbed amount is proportional to the logarithm of the bulk concentration (Kano et al., 2000).

The empirical Freundlich equation is written as follows:

$$q_e = K_f C_e^{1/n} \dots \dots \dots (2-7)$$

where:

q_e : amount of adsorbate adsorbed per unit mass of adsorbent, (mg adsorbate/g).

K_f : Freundlich capacity factor, (mg/g) (L/mg)^{1/n}

C_e : equilibrium concentration of adsorbate in solution after adsorption, (mg/L)

(1/n): Freundlich intensity parameter.

the linear form of equation above rewritten as:

$$\text{Log } (q_e) = \text{log } K_f + 1/n \text{ log } C_e \dots \dots \dots (2-8)$$

The constants in the Freundlich isotherm can be determined by plotting log (q_e) versus log C_e , a straight line is obtained with a slope of 1/n, and log K_f is the intercept.

2.6.3.2 Langmuir isotherm

In 1916 Langmuir proposed another adsorption isotherm known as Langmuir adsorption isotherm. It's probably the most widely used model. This model is based on four assumptions (Sohn and Kin, 2004):

- 1 - Adsorption cannot proceed beyond monolayer coverage; all sorbent surface sites are equivalent and can accommodate.
- 2-Adsorbed molecules do not interact.
- 3-All adsorption occurs through the same mechanism.
- 4-At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Langmuir model can be expressed by:

$$q_e = K_L q_m C_e / (1 + K_L C_e) \dots\dots\dots(2-9)$$

where:

q_e : amount of adsorbate adsorbed per unit mass of adsorbent, (mg adsorbate/g).

q_m : maximum adsorption capacity of the adsorbent, (mg/g).

K_L : Langmuir's constant, (L/mg)

C_e : equilibrium concentration of adsorbate in solution after adsorption, (mg/L)

The linear form of equation above rewritten as:

$$1/(q_e) = 1/K_L q_m (1/C_e) + (1/q_m) \dots\dots\dots(2-10)$$

The constants in the Langmuir isotherm can be determined by plotting $1/(q_e)$ versus $1/C_e$. In which the value of q_m obtained from the intercept, which is $(1/q_m)$, and the value of K_L from the slope which is $(1/K_L q_m)$.

2.6.3.3 Adsorption of Cypermethrin

A Study by Ismail, Mazlinda and Tayeb (2013) were conducted to determine the adsorption and mobility of cypermethrin in peat and silt clay soils. Adsorption studies showed that adsorption of cypermethrin into soil fit the Freundlich adsorption isotherm. The Freundlich adsorption distribution coefficients [K_{ads}] for peat soil was 205 1/kg and for silt clay soil was 140 1/kg indicated that cypermethrin was more easily adsorbed in peat soil. while K_{oc} values of cypermethrin were 256 for peat soil and 1643 for silt clay soil. In the mobility study, the results showed that mobility of this insecticide was greater in peat soil than silt clay soil.

Another study by Layla, Anis, and Zaki (2015) were conducted to determine the adsorption of cypermethrin on eight agricultural soil samples. The kinetics study investigated that adsorption processes of cypermethrin follows the first order rate law. Values of K_F ranged from 9.204-46.374 ml/g. The maximum amount of pesticides adsorption (q_m $\mu\text{g/g}$) ranged from 6.285-53.19. and the K_d values for cypermethrin were ranged from 7.298-20.254 ml/g.

Cypermethrin is expected to bind strongly to organic carbon and have little mobility in soil (K_{oc} values ranged from 20,800 to 385,000 L/kg), and therefore it is not likely to leach into groundwater. Due to its relatively low mobility, cypermethrin is most likely to reach adjacent bodies of water via spray drift, through runoff events accompanied by soil erosion, or in runoff from outdoor impervious surfaces. Cypermethrin is moderately persistent in the

environment and degrades through a combination of biotic and abiotic mechanisms (USEPA, 2006).

2.6.3.4 Adsorption of Chlorfenapyr

Previous research by Sun Xiao-yan, Yin Xing and Wang Ming-hua (2013) were conducted to determine the adsorption and mobility of chlorfenapyr in different soil samples. The results showed that the sorption isotherm could be well described by Freundlich equation. Adsorption coefficient (K_F) of chlorfenapyr on soils (red earth of Jiangxi, yellow-brown earth of Nanjing and black earth of northeast) were 469.87, 550.94 and 607.16, respectively. The adsorption of chlorfenapyr was dominated by physical adsorption. The results of mobility of chlorfenapyr display non-mobile and non-leaching.

Based on review of environmental fate data (requirements listed under 40 CFR § 158.290) by EPA's Environmental Fate and Effects Division (EFED), chlorfenapyr is considered immobile and has a relatively high affinity for soil. The K_{oc} values for chlorfenapyr ranged from 10000 to 14762 with an average of 11960 L/Kg, indicating that chlorfenapyr is strongly adsorbed by soil. Therefore, in spite of its persistence in the environment, chlorfenapyr is not expected to be a groundwater concern. The mobility characteristics exhibited by this compound in both the laboratory and field are not those generally associated with compounds found in groundwater (USEPA, 1998).

CHAPTER 3 MATERIALS AND METHODS

3.1 Soil

3.1.1 Soil Sampling

The soil samples were selected from two agricultural locations with depth (0-30) cm in Tafilah-Jordan. The locations are Ais, Abur (Figure (3.1)). They are suitable sites with shallow groundwater aquifer and intensive agriculture practices.

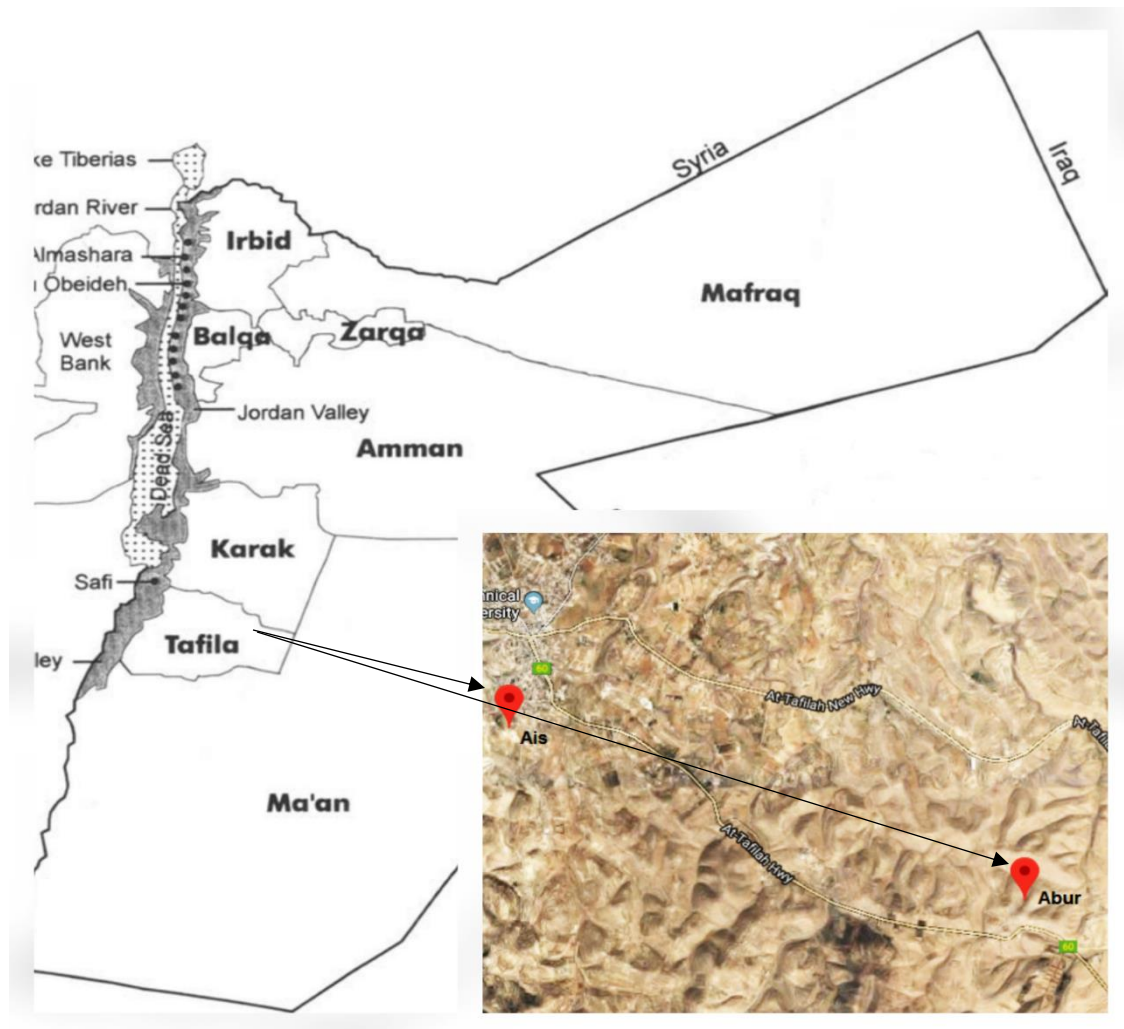


Figure (3.1): The locations of the selected soil samples.

The soils were identified and classified based on sieve analysis and hydrometer test (ASTM D422), The organic matter of the soil was determined by Walkley-Black chromic acid wet oxidation method. The soil pH was measured by using a direct reading of a pH meter. The specific gravity was determined by pycnometer method (ASTM D854). The properties of the collected soils are given in Table (3.1). The soils were sieved through IS (International Standard) sieve No. 10 (2mm). The fraction passing through the sieve was collected and preserved in air tight plastic containers for further analysis.

3.1.2 Soil characteristics

The texture and organic matter contents for each soil was determined in the laboratory. The methods used are described below:

3.1.2.1 Total organic matter contents " T.O.M "

A 1 g sample of dried soil was placed in 250 mL conical flask, 10 mL of 1.0 N $K_2Cr_2O_7$ and 20 mL of concentrated H_2SO_4 were added gradually for 1 minute. After 30 minutes 200 mL of distilled water and 0.30 mL of 0.025M ortho-phenanthroline- ferrous complex were added. A greenish cast color to dark blue green was observed. The contents titrated against 0.40 N ferrous sulfate solution, until the color changed from blue to orange. A blank of $K_2Cr_2O_7$ solution was treated as samples (Walkley and Black, 1934).

The following equation was used to calculate the T.O.M %:

$$\text{Organic carbon (\%)} = (0.003 \text{ g} \times N \times 10 \text{ ml} \times (1-T/S) \times 100) / \text{sample dry weight (g)}.$$

$$\text{Organic carbon (\%)} = 3(1-T/S) / \text{sample dry weight (g)}.$$

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).

T.O.M % = $1.72 \times \text{organic carbon \%}$.

3.1.2.2 Texture (Hydrometer Method)

A 50-g sample of dried soil was placed in a 1-liter beaker, 125 mL of 4% solution of sodium hexametaphosphate (calgon) (prepared by adding 40g of calgon to 1000 mL of distilled water and mixed thoroughly) was added and allowed to soak for about 8 to 12 hours. In the second day, the mixture was mixed well and poured into mixer cup to make it about two thirds full, the mixture then was poured in to a second graduated 1000 mL cylinder, then filled with distilled water up to the 1000 mL mark. The hydrometer readings were taken at cumulative times: $t = 0.25 \text{ min}, 0.5 \text{ min}, 1 \text{ min}, 2 \text{ min}, 4 \text{ min}, 8 \text{ min}, 15 \text{ min}, 30 \text{ min}, 1 \text{ hr}, 2 \text{ hr}, 4 \text{ hr}, 24 \text{ hr}$.

A Table was prepared in which the first column was the time (min), the second one was the hydrometer readings (R), the third was (R_{cp}) which is the corrected hydrometer reading for calculation of percent finer = $R + F_T - F_z$.

Column four was the percent finer = $(a * R_{cp}) / (W_s * 100)$, where W_s = dry weight (g) of soil used for the hydrometer analysis, a = correction for specific gravity = $G_s (1.65) / (G_s - 1) 2.65$.

Column five is the (R_{cL}) = corrected hydrometer reading for determination of effective length = $R + F_m$.

Column 6 is the determined L (effective length corresponding) to the values of R_{cL} .

Column 7 is the determined (A) values.

Column 8 is the determined $((D) \text{ (mm)}) = A\sqrt{L(\text{cm}) / t(\text{min})}$

A graph was plotted between % finer Vs. D (mm) on log scale. From the graph: % silt the area between 0.075- 0.002.

% clay is the area < 0.002, (Day, 1978).

Table (3.1): Properties of different soils used for the present study

Soil properties	Soil (1) (Ais)	Soil (2) (Abur)
Specific gravity	2.64	2.63
pH Value	9.30	9.31
Clay (%)	2	3
Silt (%)	7	9
Sand (%)	91	88
Organic matter (%)	1.77	2.02

3.2 Chemicals

All chemicals used were analytical grade. cypermethrin and chlorfenapyr were purchased from Sigma Aldrich Ltd.

3.3 Cypermethrin and chlorfenapyr standard solutions

A stock 10000 ppm solution of cypermethrin and chlorfenapyr was prepared by transferring exactly 1 g of cypermethrin and chlorfenapyr into a 100-ml volumetric flask. The volume was completed to the mark with acetonitrile.

3.4 Reaction vessels

Pyrex conical flasks were used in this study. The flasks were cleaned with distilled water and acetone, then dried at 110°C for 0.5 hour prior to use.

3.5 Instrumentation

The instrument used for analysis was Varian CP-3800 GC MS (made in USA), shaker and centrifuge.

3.6 Adsorption study

3.6.1 Kinetic study

The adsorption kinetic study was carried out in batch mode using 250 mL conical flask with 5 g of appropriate soil (listed in Table 3.1) and 5 ml of 10,000 ppm of technical cypermethrin (200 ppm) and 1.5 ml of 10,000 ppm of technical chlorfenapyr (60 ppm) solution and completing the volumes to the mark with water. Sorbent masses were accurate to ± 0.0001 g and solution volumes to ± 0.5 ml. The experiments were conducted for the soils on a shaker at 150 rpm for a period of 24 h at room temperature ($25 \pm 2^\circ\text{C}$). From the flasks, 10 ml (cypermethrin) and 5 ml (chlorfenapyr) of sample was collected at time intervals of 0.083, 0.25, 0.5, 1, 2, 4, 6 and 24 h. The collected samples were extracted, filtered using $0.22\ \mu\text{m}$ syringe filters and analyzed by GC-MS.

3.6.2 Equilibrium study

Adsorption equilibrium studies were conducted for the two soils with an adsorbent quantity of 5 g with technical cypermethrin concentrations of 50, 100, 150, and 200 ppm and chlorfenapyr concentrations of 15, 30, 45 and 60 ppm in 250 ml conical flasks and completing the volumes to the mark with water. the reaction mixtures were agitated in shaker at 150 rpm for 2 h (estimated equilibrium time) for cypermethrin and chlorfenapyr at $25 \pm 2^\circ\text{C}$. After that, 10 ml (cypermethrin) and 5 ml (chlorfenapyr) of sample was collected from each conical

flask, the collected samples were extracted, filtered using 0.22 μm syringe filters and analyzed using GC-MS.

3.6.3 Extraction and Filtration of soil samples:

The method used to extract cypermethrin from the soil samples was QuEChERS method (Schenck and Hobbs, 2004), in which 10 ml of sample was placed in a 50-ml centrifuge tube then 10 ml of acetonitrile were added to the sample, shaken for 1 minute, until uniform, then 4 g MgSO_4 , 1 g NaCl and 0.5 g sodium citrate were added and vigorously shaken for 2 minutes. On the other hand, the method used to extract chlorfenapyr from soil was solvent extraction (EPA, method 1664), in which 5 ml of sample was placed in a 20-ml centrifuge tube then 5 ml of n-hexane were added to the sample. After that all samples were centrifuged for 5 minutes at 3000 rpm, then filtered using 0.22 μm syringe filters.

3.6.4 Calibration curve for cypermethrin

Standard solutions of cypermethrin 10, 25, 50, 100, 150, 200, 250 ppm were prepared by transferring 0.1, 0.25, 0.5, 1, 1.5, 2 and 2.5 mL respectively, from 10000 ppm standard solution of cypermethrin into 100 ml volumetric flasks and completing the volumes to the mark with water.

3.6.5 Calibration curve for chlorfenapyr

Standard solutions of chlorfenapyr 2.5, 5, 10, 20, 30, 40, 60, 80 ppm were prepared by transferring 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 ml respectively, from 10000 ppm standard solution of chlorfenapyr into 100 ml volumetric flasks and completing the volumes to the mark with water.

3.6.6 GC Analysis

Varian 3800 gas chromatography equipped with Varian 2000 mass spectrometer detector with Varian 8400 autosampler, Varian capillary column CP-Sil 8 CB (25m X 0.25mm id, 0.12 μ m film thickness), the operating temperature were: injection port 250 $^{\circ}$ C oven programmed initially 50 for 1min and then increased to 250 $^{\circ}$ C at the rate of 15 $^{\circ}$ C /min and maintained for 11.34 min detector trap temperature 150 $^{\circ}$ C. the carrier gas was high purity helium (He, 99.999%) with a flow rate of 1.0 mL/min. injection volume 1 μ L.

CHAPTER 4

RESULTS AND DISSCUSSION

4.1 Calibration curve

4.1.1 Calibration curve for cypermethrin

A linear relationship was obtained between the response Table (4.1) and the concentration of cypermethrin (Figure (4.1)). The relative standard deviation for 6 measurements of (200) ppm is (1.05 %) with 98.59% recovery. A representative chromatogram of cypermethrin is shown in Figure (4.2).

Table (4.1): Calibration curve for cypermethrin.

Concentration (ppm)	Response
10	644494
25	887250
50	1345092
100	2693134
150	4102496
200	5438004
250	7158979

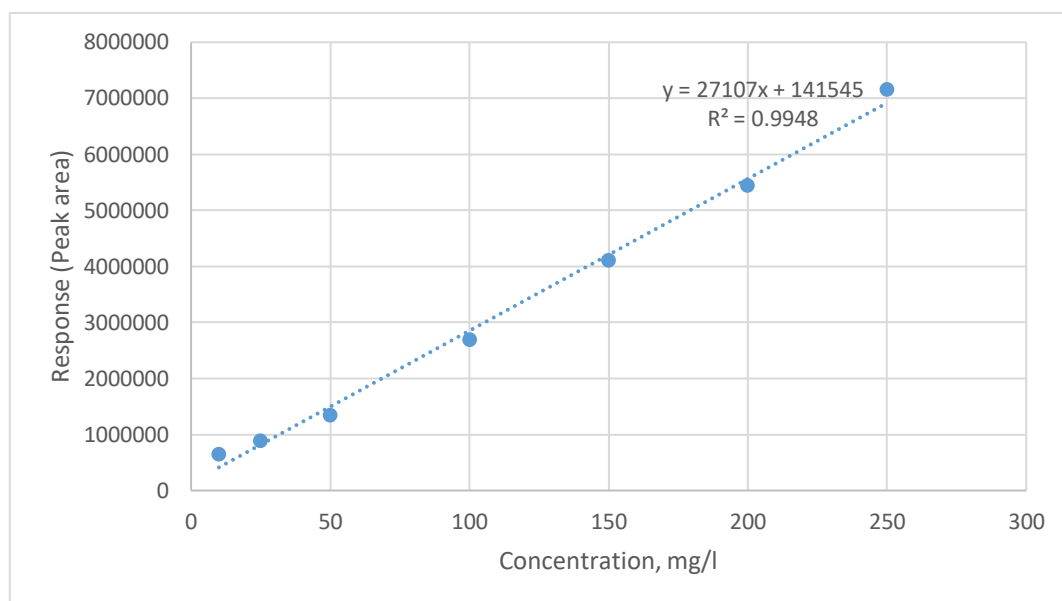
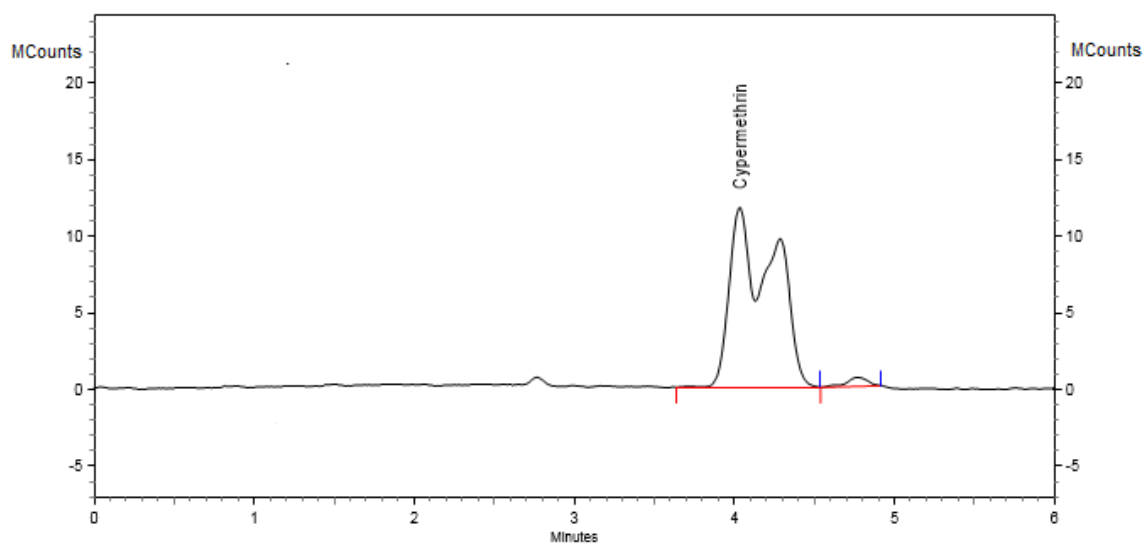


Figure (4.1): Calibration curve of cypermethrin



Results				
Pk #	Name	Retention Time	Area	Concentration
1	Cypermethrin	4.033	887250	25.000 CAL

Figure (4.2): A representative chromatogram of cypermethrin

4.1.2 Calibration curve for chlorfenapyr

A linear relationship was obtained between the response (Table (4.2)) and the concentration of chlorfenapyr (Figure (4.3)). And the relative standard deviation for 6 measurements of (60) ppm is (2.67 %) with 84.11% recovery. A representative chromatogram of chlorfenapyr is shown in Figure (4.4).

Table (4.2): Calibration curve for chlorfenapyr.

Concentration (ppm)	Response
2.5	629459
5	1258918
10	2517837
20	4962529
30	8098495
40	11612242
60	18228473
80	25102050

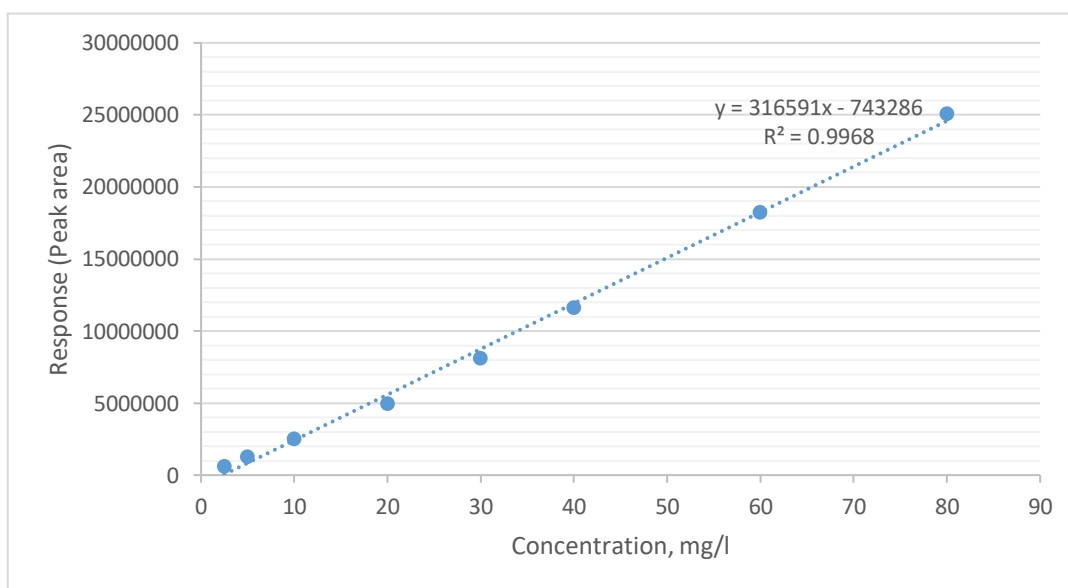


Figure (4.3): Calibration curve for chlorfenapyr

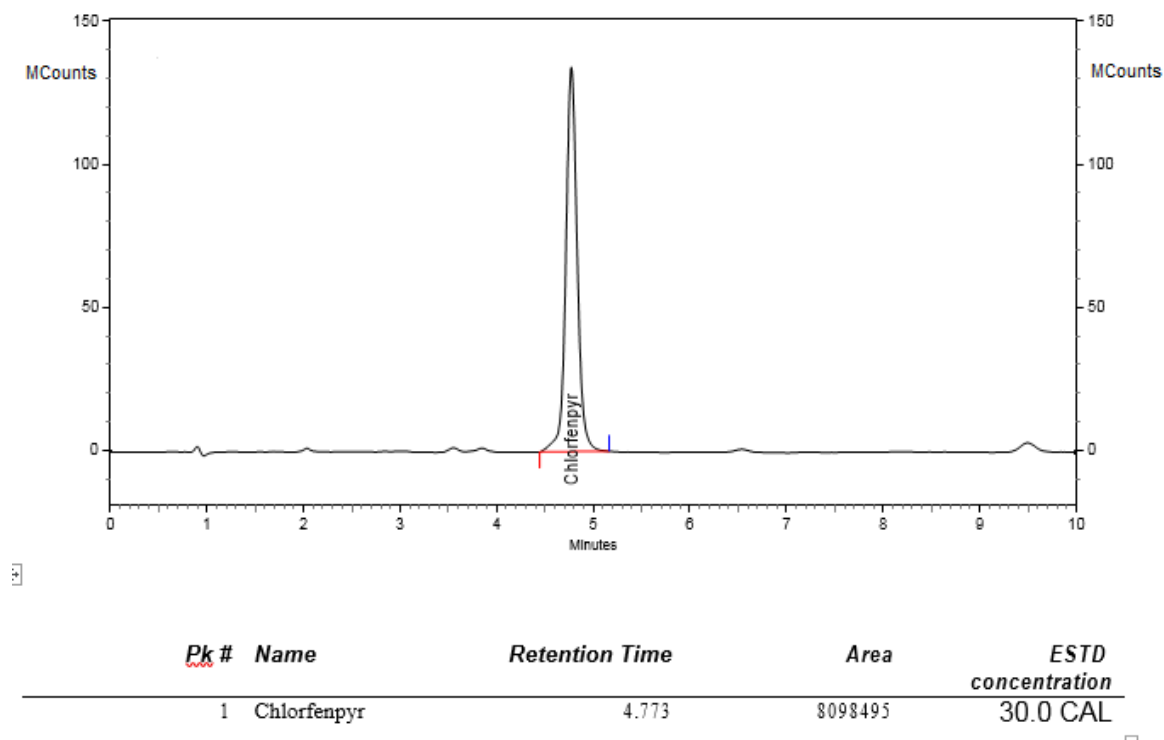


Figure (4.4): A representative chromatogram of chlorfenapyr

4.2 Adsorption

4.2.1 Kinetic study

In general, the kinetics of adsorption are analyzed using pseudo first-order model (Lagergren, 1898), pseudo second-order model (Ho et al., 2000). The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2 , values close or equal to 1) and the mean squared error (MSE, values closer to zero). A relatively high R^2 value and closer value of MSE to zero indicates that the model successfully describes the kinetics of adsorbate adsorption. Batch sorption tests are carried out at certain experimental conditions for kinetics' testing.

4.2.1.1 Kinetic study for cypermethrin

The adsorption kinetics exhibited an immediate rapid adsorption and reached pseudo adsorption equilibrium within a short period of 2 hrs in both soils (Figure (4.5)). After pseudo equilibrium, less than 2% variation of cypermethrin concentration in the adsorbate was observed even after 24 hrs.

Beck and Jones (1996) studied the sorption of atrazine and isoproturon and they found that, the herbicides were removed from the solution within the first hour of the 24 hrs of sorption experiments. The rapid initial adsorption of cypermethrin is a surface phenomenon. Due to hydrophobic nature of cypermethrin, the vacant sites in the soil particles were filled up rapidly in the initial stages and followed a linear variation. This is followed by a slow migration and diffusion of the compound (the rate of adsorption decreased drastically and reached the steady state) into the organic matter matrix and mineral structure (Gao et al., 1998).

From the results it is clear that, the sorption of cypermethrin in soils is rapid in the initial period and the portion of pesticide participating in the long-term behavior is insignificant as compared to that participating in the preliminary phase of rapid sorption.

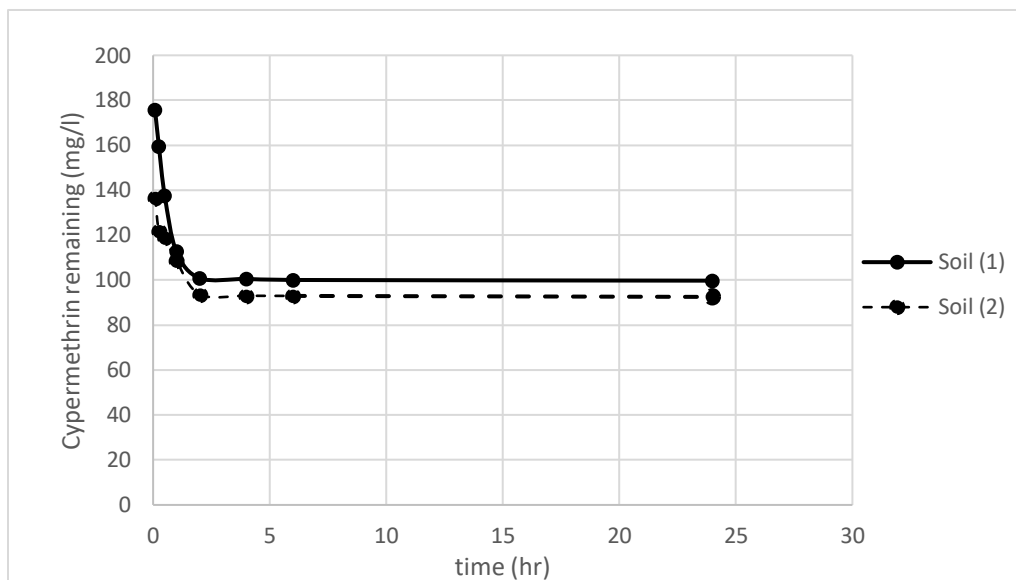


Figure (4.5): Kinetics of cypermethrin adsorption on the two soil samples

The kinetic rates were estimated by pseudo first order model, and pseudo second order model, given in Equations below respectively.

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

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e) \cdot t$$

where q_e is the amount of adsorbate sorbed at equilibrium; q_t is the amount of adsorbate sorbed on the surface of the sorbent at any time; k is the rate constant of sorption; and t is the time.

The data of first order and second order reaction kinetics are shown in Tables (4.3-4.7), and the plots in Figures (4.6-4.8).

Table (4.3): Pseudo-first-order reaction kinetic for cypermethrin in soil (1) (Ais)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage $R_{em} \%$	Amount Adsorbed q_t (mg/g)	$\log(q_e - q_t)$
0.0833	200	175.75	12	1.2125	0.575
0.25	200	159.42	20	2.029	0.469
0.5	200	137.51	31	3.1245	0.267
1	200	112.69	44	4.3655	-0.216
2	200	100.89	50	4.9555	-1.745
4	200	100.53	50	4.9735	-
6	200	100.07	50	4.9965	-
24	200	99.76	50	5.012	-

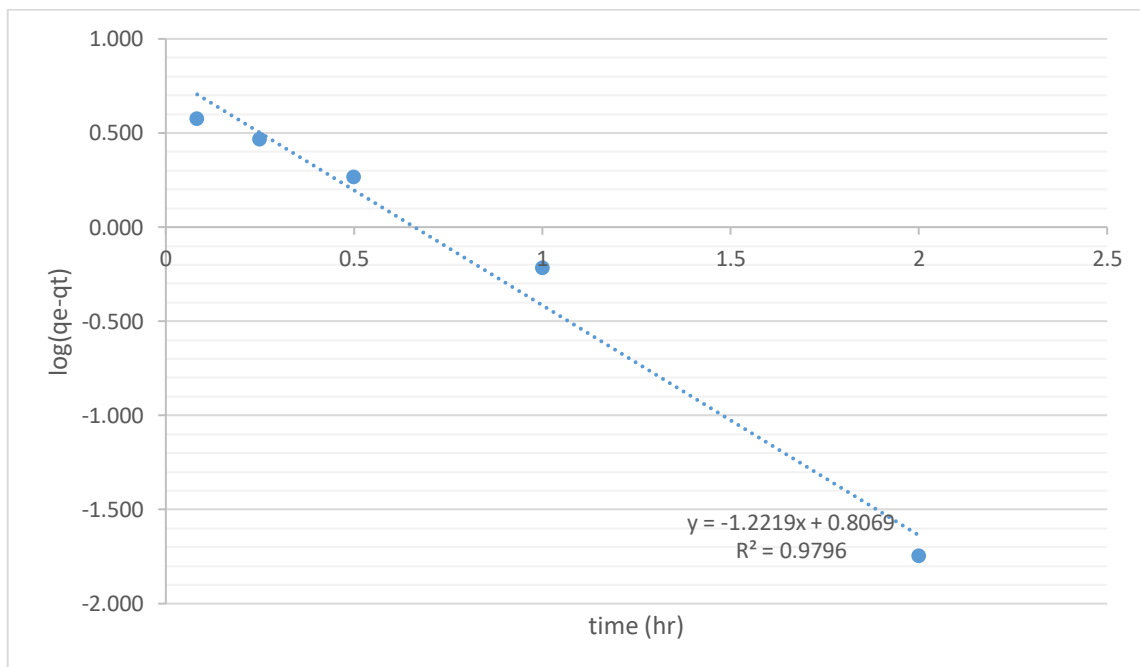
**Figure (4.6): Plot of $\log(q_e - q_t)$ versus time for cypermethrin in soil (1) (Ais)**

Table (4.4): Pseudo-first-order reaction kinetic for cypermethrin in soil (2) (Abur)

Time	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage R_{em} %	Amount Adsorbed q_t (mg/g)	$\log(q_e - q_t)$
0.0833	200	136.68	32	3.166	0.339
0.25	200	121.63	39	3.9185	0.155
0.5	200	119.01	40	4.0495	0.113
1	200	108.56	46	4.572	-0.110
2	200	93.61	53	5.3195	-1.553
4	200	93.05	53	5.3475	-
6	200	92.98	54	5.351	-
24	200	92.54	54	5.373	-

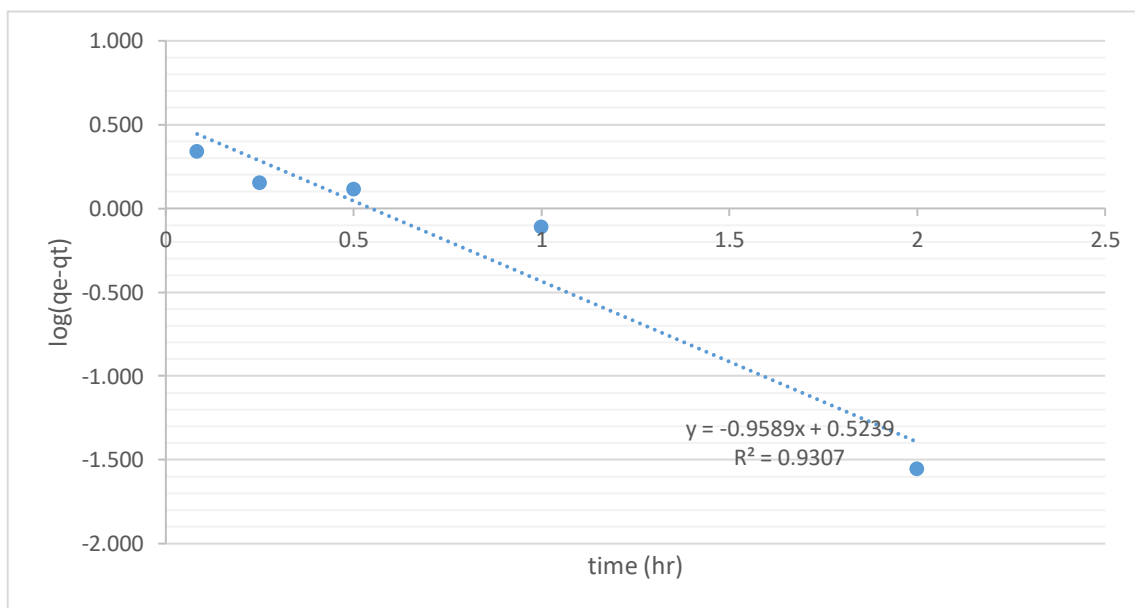
**Figure (4.7): Plot of $\log(q_e - q_t)$ versus time for cypermethrin in soil (2) (Abur)**

Table (4.5): Pseudo-second-order reaction kinetic for cypermethrin in soil (1) (Ais)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage R_{em} %	Amount Adsorbed q_t (mg/g)	t/q_t
0.0833	200	175.75	12	1.2125	0.0687
0.25	200	159.42	20	2.029	0.1232
0.5	200	137.51	31	3.1245	0.1600
1	200	112.69	44	4.3655	0.2291
2	200	100.89	50	4.9555	0.4036
4	200	100.53	50	4.9735	0.8043
6	200	100.07	50	4.9965	1.2008
24	200	99.76	50	5.012	4.7885

Table (4.6): Pseudo-second-order reaction kinetic for cypermethrin in soil (2) (Abur)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage R_{em} %	Amount Adsorbed q_t (mg/g)	t/q_t
0.0833	200	136.68	32	3.166	0.0263
0.25	200	121.63	39	3.9185	0.0638
0.5	200	119.01	40	4.0495	0.1235
1	200	108.56	46	4.572	0.2187
2	200	93.61	53	5.3195	0.3760
4	200	93.05	53	5.3475	0.7480
6	200	92.98	54	5.351	1.1213
24	200	92.54	54	5.373	4.4668

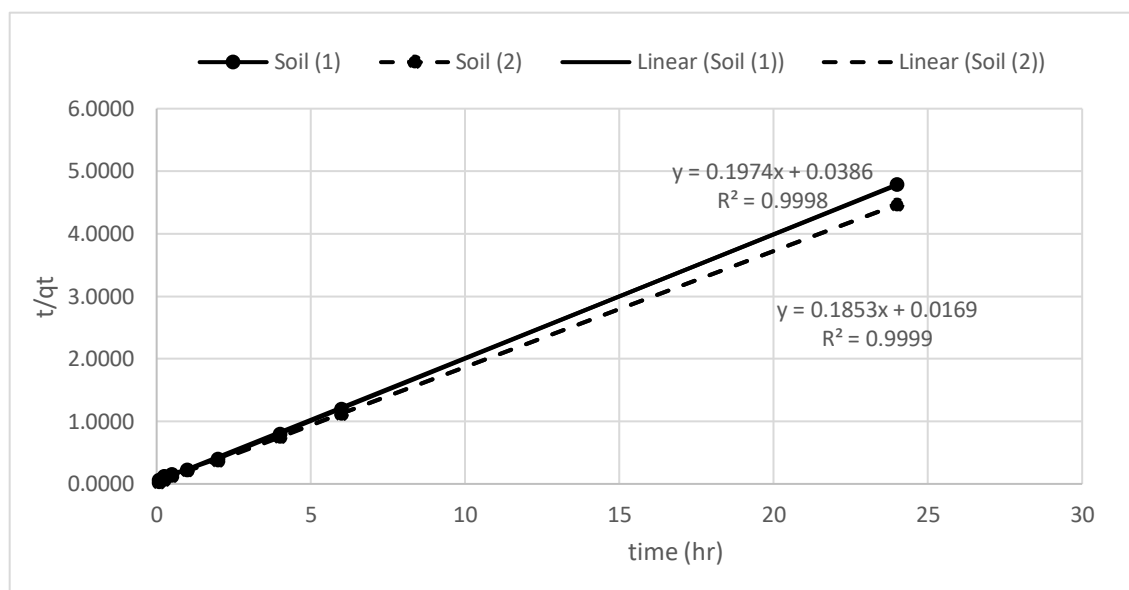


Figure (4.8): Plot of t/q_t versus time for cypermethrin in two soils

As we see from Tables (4.3-4.6) and Figures (4.6-4.8), the first 5 minutes has a low percent removal about 12 % only in soil (1) and about 31% in soil (2), but after about an hour of adsorption the percent removal rise to reach 43 % in soil (1) and about 45 % in soil (2) and its rises slowly. and after 2 hrs the percent removal increased even more to about 50 % in soil (1) and 53% in soil (2), then equilibrium occurs at about 2 hrs.

Table (4.7): adsorption rate constants, experimental and calculated q_e values for the pseudo-first and -second order reaction kinetics for cypermethrin

Type of soil	First order					Second order				
	K_1 (hr ⁻¹)	log q_e	q_e (mg/g)	MSE	R^2	K_2 (g/mg hr)	q_e (mg/g)	MSE	R^2	q_{exp} (mg/g)
Soil (1)	2.814	0.8069	6.411	0.0148	0.9796	1.009	5.0658	0.0005	0.9998	4.973
Soil (2)	2.208	0.5239	3.341	0.0326	0.9307	2.031	5.3966	0.0001	0.9999	5.348

From the results, it's clear that the rate of adsorption of cypermethrin in soil (2) (2.0317 g/mg.hr) is higher than in soil (1) (1.009 g/mg.hr).

Since, the difference between q_e calculated and q_e experimental values is very small and the correlation coefficient (R^2) values for the second order reaction equation plots are higher than that of the first order reaction kinetic, and since the values of MSE in the second order reaction are smaller than that of the first order reaction, it is seen that the adsorption of cypermethrin in the two soils well described by the second order reaction kinetic which suggest the process of adsorption is chemisorption. 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).

4.2.1.2 Kinetic study for chlorfenapyr

The adsorption kinetics exhibited an immediate rapid adsorption and reached pseudo adsorption equilibrium within a short period of 2 hrs. in both soils (Figure (4.9)). After pseudo equilibrium, less than 4% variation of chlorfenapyr concentration in the adsorbate was observed even after 24 h.

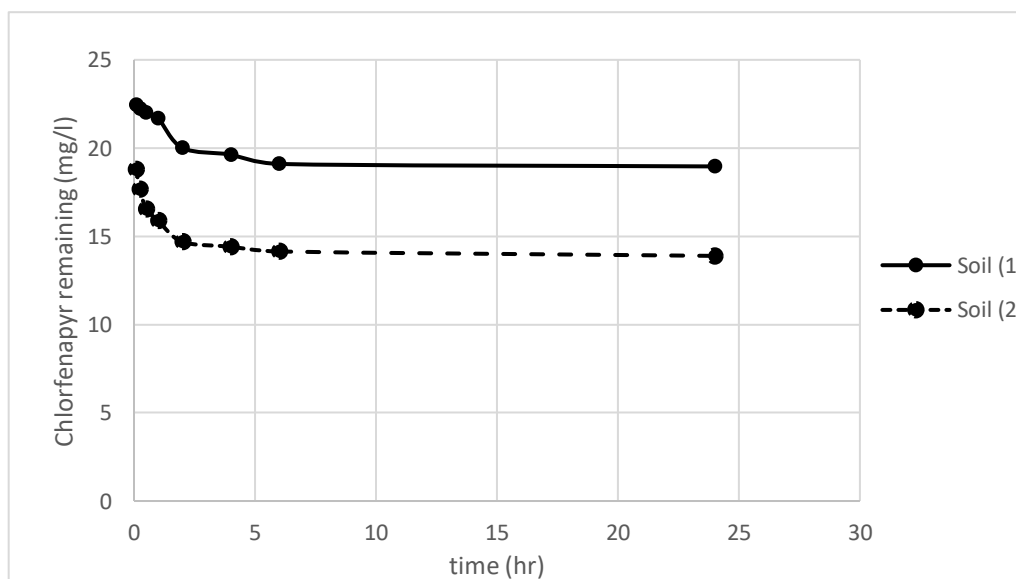


Figure (4.9): Kinetics of chlorfenapyr adsorption on the two soil samples

The data of first order and second order reaction kinetics are shown in Tables (4.8-4.12), and the plots in Figures (4.10-4.12).

Table (4.8): Pseudo-first-order reaction kinetic for chlorfenapyr in soil (1) (Ais)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage R_{em} %	Amount Adsorbed q_t (mg/g)	$\log(q_e - q_t)$
0.0833	60	22.44	63	1.878	-0.777
0.25	60	22.24	63	1.888	-0.804
0.5	60	22	64	1.9	-0.839
1	60	21.68	64	1.916	-0.889
2	60	20.01	67	1.9995	-1.342
4	60	19.63	67	2.0185	-1.577
6	60	19.1	68	2.045	-
24	60	18.96	68	2.052	-

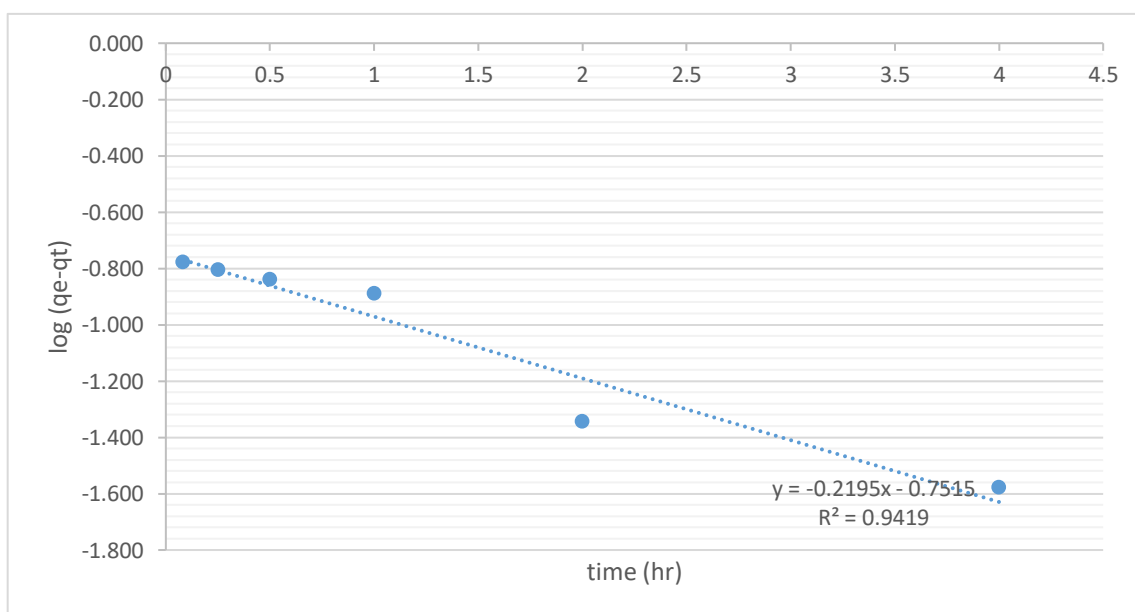


Figure (4.10): Plot of $\log(q_e - q_t)$ versus time for chlorfenapyr in soil (1) (Ais)

Table (4.9): Pseudo-first-order reaction kinetic for chlorfenapyr in soil (2) (Abur)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage $R_{em} \%$	Amount Adsorbed q_t (mg/g)	$\log(q_e - q_t)$
0.0833	60	18.79	69	2.0605	-0.660
0.25	60	17.69	71	2.1155	-0.785
0.5	60	16.55	72	2.1725	-0.971
1	60	15.89	74	2.2055	-1.131
2	60	14.69	76	2.2655	-1.854
4	60	14.41	76	2.2795	-
6	60	14.14	76	2.293	-
24	60	13.89	77	2.3055	-

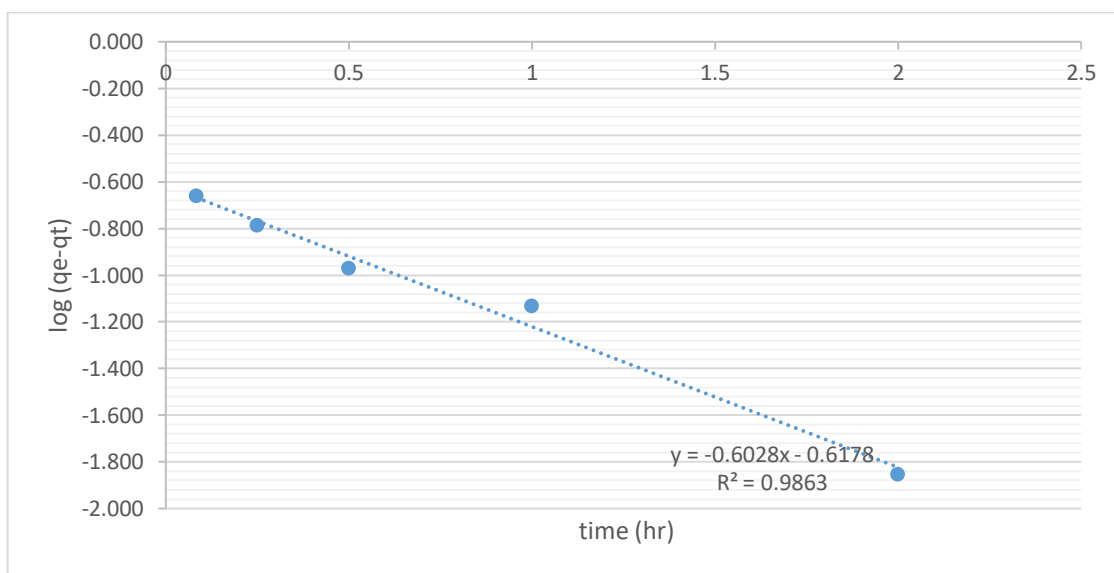
**Figure (4.11): Plot of $\log(q_e - q_t)$ versus time for chlorfenapyr in soil (2) (Abur)**

Table (4.10): Pseudo-second-order reaction kinetic for chlorfenapyr in soil (1) (Ais)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage R_{em} %	Amount Adsorbed q_t (mg/g)	t/q_t
0.0833	60	22.44	63	1.878	0.0444
0.25	60	22.24	63	1.888	0.1324
0.5	60	22	64	1.9	0.2632
1	60	21.68	64	1.916	0.5219
2	60	20.01	67	1.9995	1.0003
4	60	19.63	67	2.0185	1.9817
6	60	19.1	68	2.045	2.9340
24	60	18.96	68	2.052	11.6959

Table (4.11): Pseudo-second-order reaction kinetic for chlorfenapyr in soil (2) (Abur)

Time (hr.)	Initial Concentration C_0 (mg/l)	Concentration at time t, C_t (mg/l)	Removal Percentage R_{em} %	Amount Adsorbed q_t (mg/g)	t/q_t
0.0833	60	18.79	69	2.0605	0.0404
0.25	60	17.69	71	2.1155	0.1182
0.5	60	16.55	72	2.1725	0.2301
1	60	15.89	74	2.2055	0.4534
2	60	14.69	76	2.2655	0.8828
4	60	14.41	76	2.2795	1.7548
6	60	14.14	76	2.293	2.6167
24	60	13.89	77	2.3055	10.4099

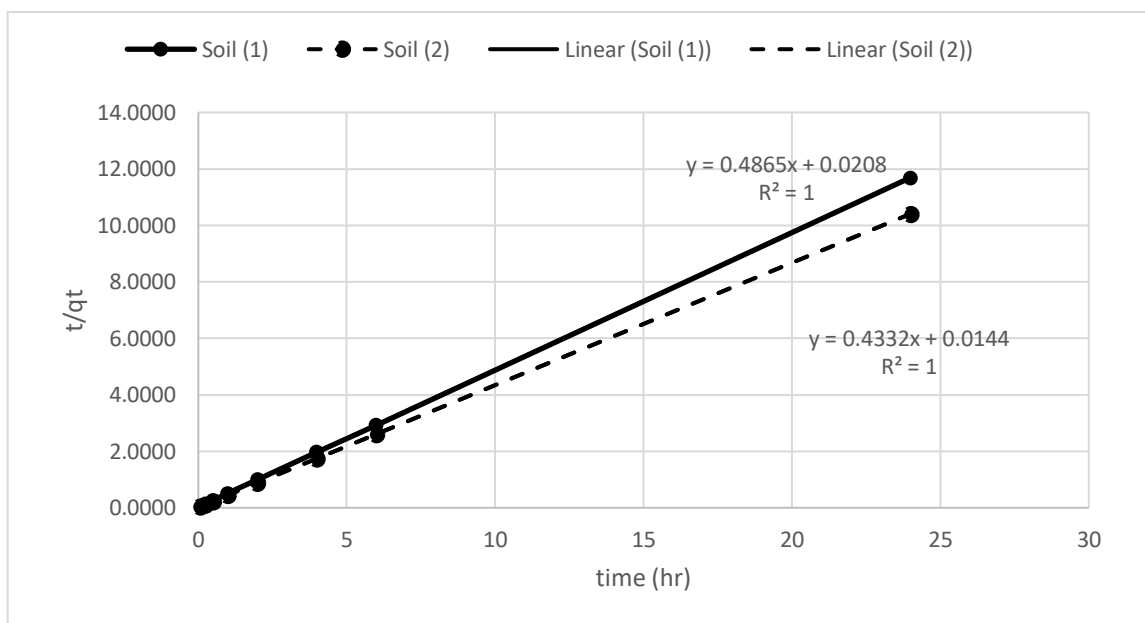


Figure (4.12): Plot of t/q_t versus time for chlorfenapyr in two soils

As we see from the Tables (4.8-4.11) and Figures (4.10-4.12), the first 5 minutes has a high percent removal about 62 % in soil (1) and about 68% in soil (2), and after about an hour of adsorption the percent removal reached 64 % in soil (1) and about 73 % in soil (2). After 2 hrs the percent removal was rising to about 66 % in soil (1) and 76% in soil (2), then equilibrium occurs at about 2 hrs.

Pseudo first and second order reaction kinetics values for chlorfenapyr in Table (4.12).

Table (4.12): adsorption rate constants, experimental and calculated q_e values for the pseudo-first and -second order reaction kinetics for chlorfenapyr

Type of soil	First order					Second order				
	K_1 (hr ⁻¹)	log q_e	q_e (mg/g)	MSE	R^2	K_2 (g/mg hr)	q_e (mg/g)	MSE	R^2	q_{exp} (mg/g)
Soil (1) (Ais)	0.505	0.7515	5.653	0.0054	0.9419	11.3789	2.0555	0.0001	1	2.045
Soil (2) (Abur)	1.388	0.6178	4.147	0.0024	0.9863	13.0321	2.3084	2.86E-05	1	2.279

From the results, it's clear that the rate of adsorption of cypermethrin in soil (2) (13.03 g/mg.hr) is higher than in soil (1) (11.38 g/mg.hr).

Since, the difference between q_e calculated and q_e experimental values is very small and the correlation coefficient (R^2) values for the second order reaction equation plots are higher than that of the first order reaction kinetic, also the values of MSE of the second order reaction are smaller than that of the first order reaction it is seen that the adsorption of chlorfenapyr in the two soils was well described by the second order reaction kinetic which suggests the process of adsorption is chemisorption.

4.2.2 Equilibrium study

4.2.2.1 Equilibrium study for cypermethrin

In order to find the short-term behavior of cypermethrin in both soils, adsorption isotherm studies were conducted at $25 \pm 2^\circ\text{C}$ with an equilibrium time of 2 hrs using Langmuir [$q_e = ((K_L q_m C_e) / (1 + K_L C_e))$] and Freundlich [$(q_e) = K_f C_e^{1/n}$] equilibrium models, where (q_e) (mg/g) is the amount of pesticide adsorbed per gram of adsorbent; C_e (mg/l) is the equilibrium concentration in solution; q_m is the maximum adsorption capacity of the adsorbent; K_L is Langmuir's constant; K_f and $1/n$ are Freundlich's adsorption coefficient and adsorption constant. The isotherm constants and the maximum adsorption capacity of the soils were calculated for (200, 150, 100, 50 ppm) cypermethrin concentrations to understand the behavior clearly (Tables 4.13 and 4.14). The relation between $1/C_e$ vs. $1/q_e$ is shown in (Figures 4.13 and 4.15), and the relationship between $\log q_e$ vs. $\log C_e$ is shown in (Figures 4.14 and 4.16).

Table (4.13): The concentration variation isotherm for the adsorption of cypermethrin in soil (1) (Ais)

Initial Concentration C_o (mg/l)	Equilibrium Concentration C_e (mg/l)	Amount Adsorbed q_e (mg/g)	$\log C_e$	$\log q_e$	$1/C_e$	$1/q_e$
200	100.91	4.9545	2.004	0.695	0.0099	0.202
150	69.22	4.039	1.840	0.606	0.0144	0.248
100	40.73	2.9635	1.610	0.472	0.0246	0.337
50	17.95	1.6025	1.254	0.205	0.0557	0.624

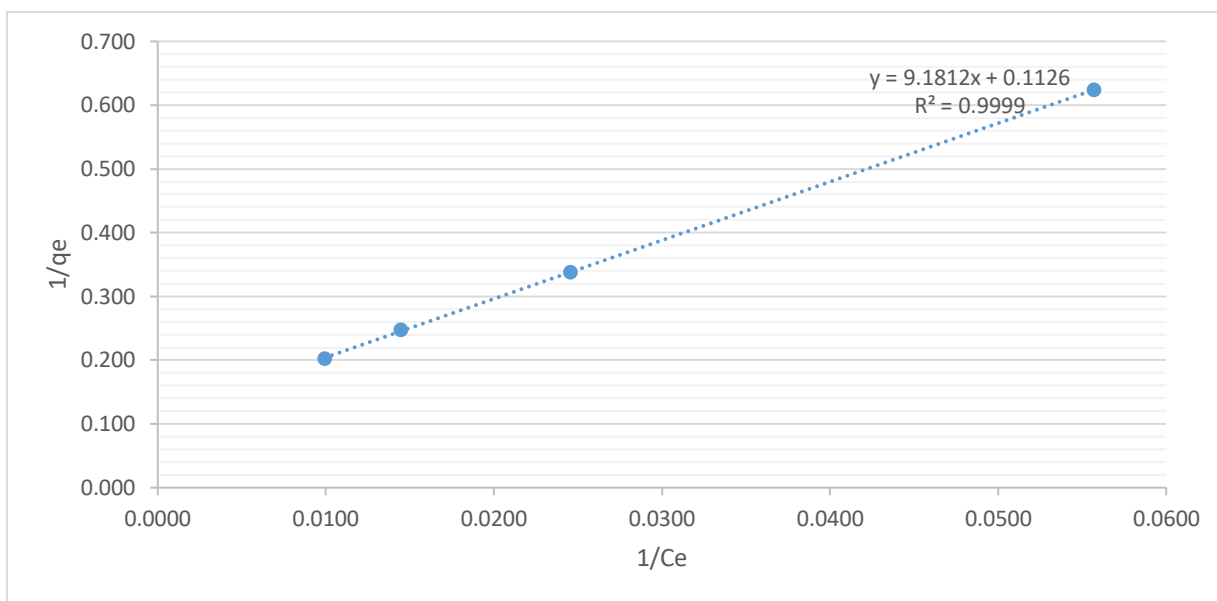


Figure (4.13): Plot of $1/q_e$ versus $1/C_e$ for cypermethrin in soil (1) (Ais)

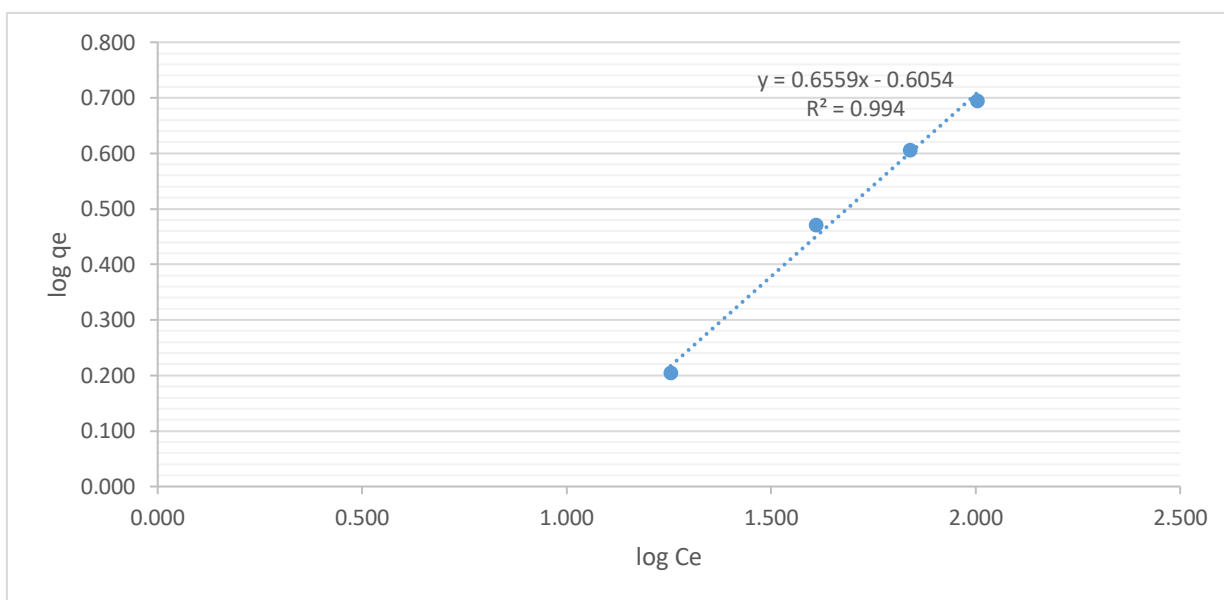


Figure (4.14): Plot of $\log q_e$ versus $\log C_e$ for cypermethrin in soil (1) (Ais)

Table (4.14): The concentration variation isotherm for the adsorption of cypermethrin in soil (2) (Abur)

Initial Concentration C_o (mg/l)	Equilibrium Concentration C_e (mg/l)	Amount Adsorbed q_e (mg/g)	$\log C_e$	$\log q_e$	$1/C_e$	$1/q_e$
200	93.174	5.3413	1.969	0.728	0.0107	0.187
150	60.912	4.4544	1.785	0.649	0.0164	0.224
100	34.966	3.2517	1.544	0.512	0.0286	0.308
50	15.12	1.744	1.180	0.242	0.0661	0.573

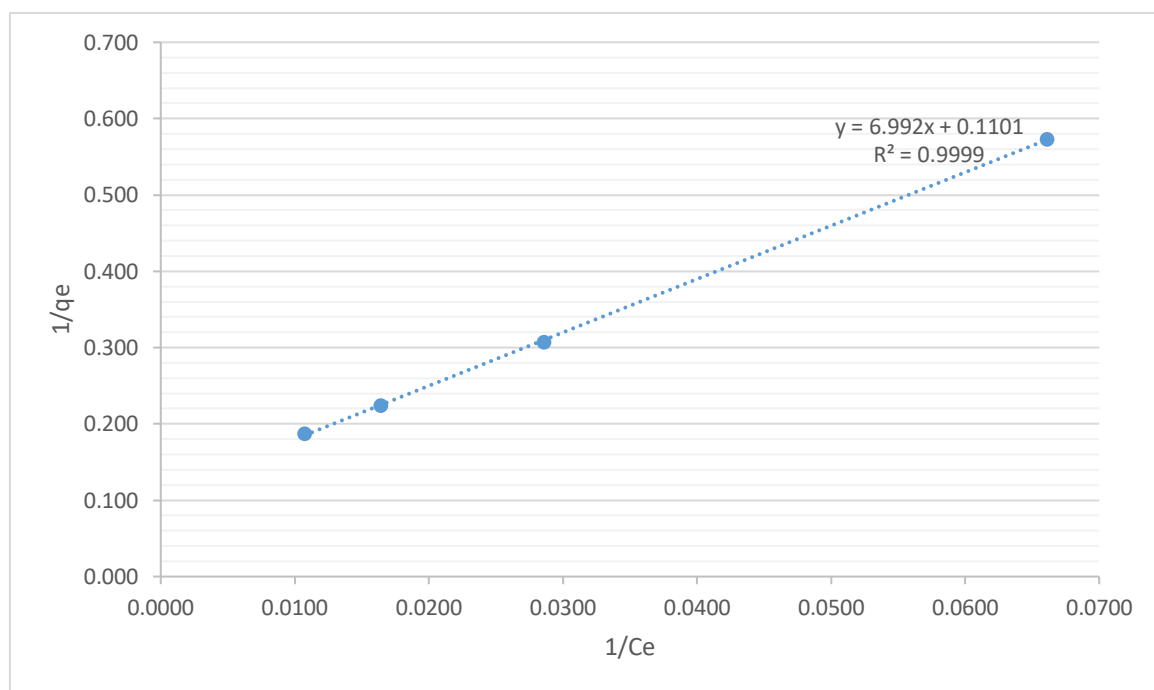


Figure (4.15): Plot of $1/q_e$ versus $1/C_e$ for cypermethrin in soil (2) (Abur)

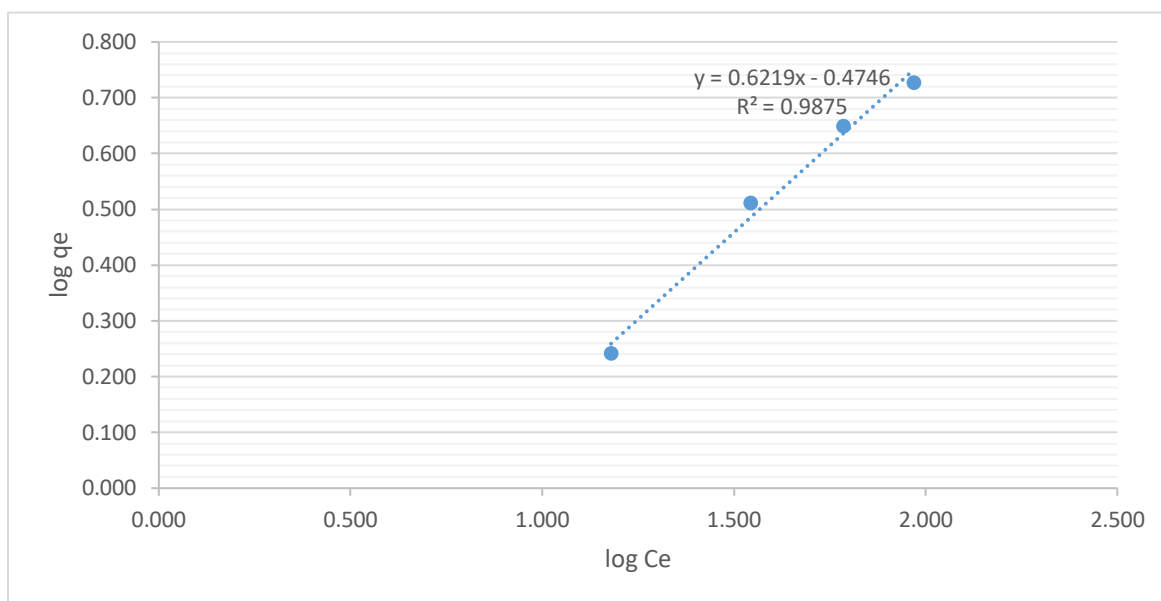


Figure (4.16): Plot of log q_e versus log C_e for cypermethrin in soil (2) (Abur)

4.2.2.2 Equilibrium study for chlorfenapyr

To find the short-term behavior of and chlorfenapyr in both soils, adsorption isotherm studies were conducted at $25 \pm 2^\circ\text{C}$ with an equilibrium time of 2 hrs for both soils. The isotherm constants and the maximum adsorption capacity of the soils were calculated for (60, 45, 30, 15 ppm) chlorfenapyr concentrations to understand the behavior clearly Tables (4.16 and 4.15).

The relation between $1/C_e$ vs. $1/q_e$ is shown in (Figs. 4.17 and 4.19), and the relationship between $\log q_e$ vs. $\log C_e$ is shown in (Figures 4.18 and 4.20).

Table (4.15): The concentration variation isotherm for the adsorption of chlorfenapyr in soil (1) (Ais)

Initial Concentration C_0 (mg/l)	Equilibrium Concentration C_e (mg/l)	Amount Adsorbed q_e (mg/g)	$\log C_e$	$\log q_e$	$1/C_e$	$1/q_e$
60	19.125	2.04375	1.282	0.310	0.052	0.489
45	15.019	1.49905	1.177	0.176	0.067	0.667
30	9.715	1.01425	0.987	0.006	0.103	0.986
15	4.791	0.51045	0.680	-0.292	0.209	1.959

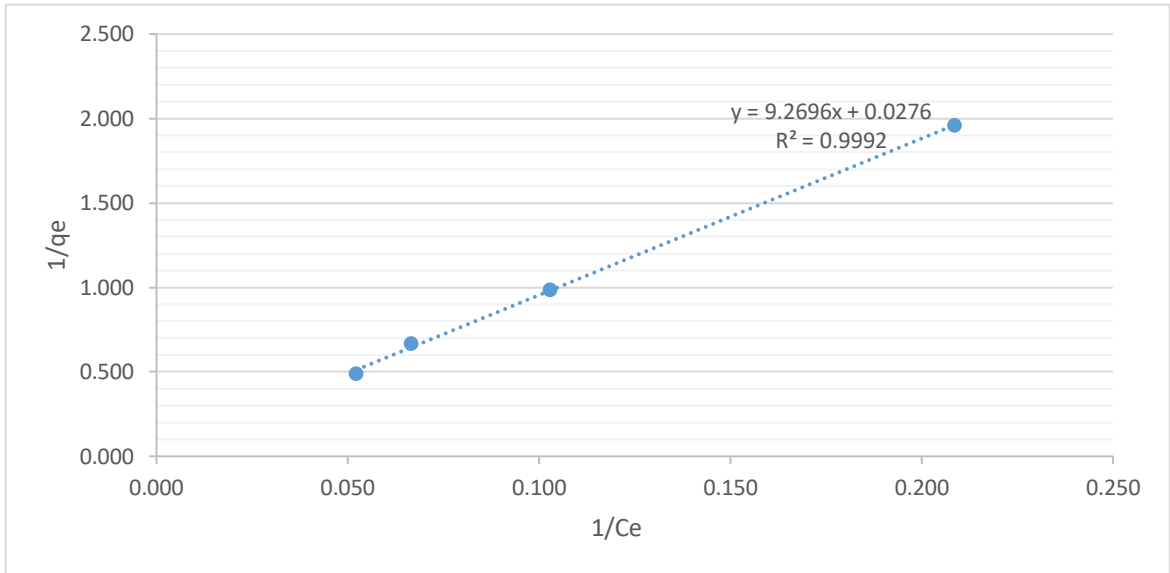


Figure (4.17): Plot of $1/q_e$ versus $1/C_e$ for chlorfenapyr in soil (1) (Ais)

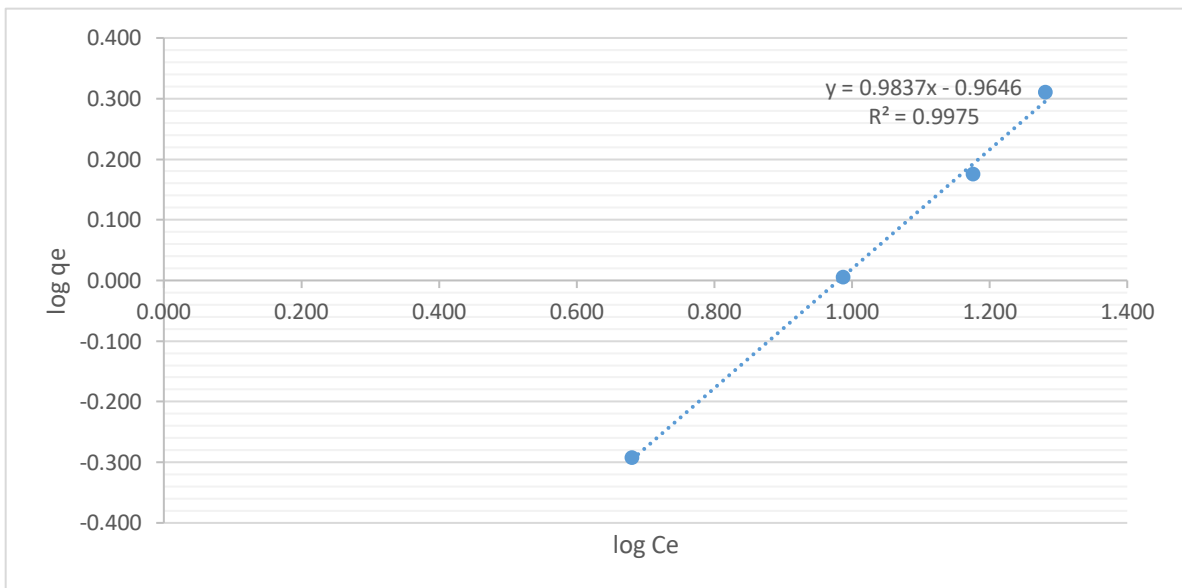


Figure (4.18): Plot of $\log q_e$ versus $\log C_e$ for chlorfenapyr in soil (1) (Ais)

Table (4.16): The concentration variation isotherm for the adsorption of chlorfenapyr in soil (2) (Abur)

Initial Concentration C_o (mg/l)	Equilibrium Concentration C_e (mg/l)	Amount Adsorbed q_e (mg/g)	$\log C_e$	$\log q_e$	$1/C_e$	$1/q_e$
60	14.114	2.2943	1.150	0.361	0.071	0.436
45	10.823	1.70885	1.034	0.233	0.092	0.585
30	7.061	1.14695	0.849	0.060	0.142	0.872
15	3.487	0.57565	0.542	-0.240	0.287	1.737

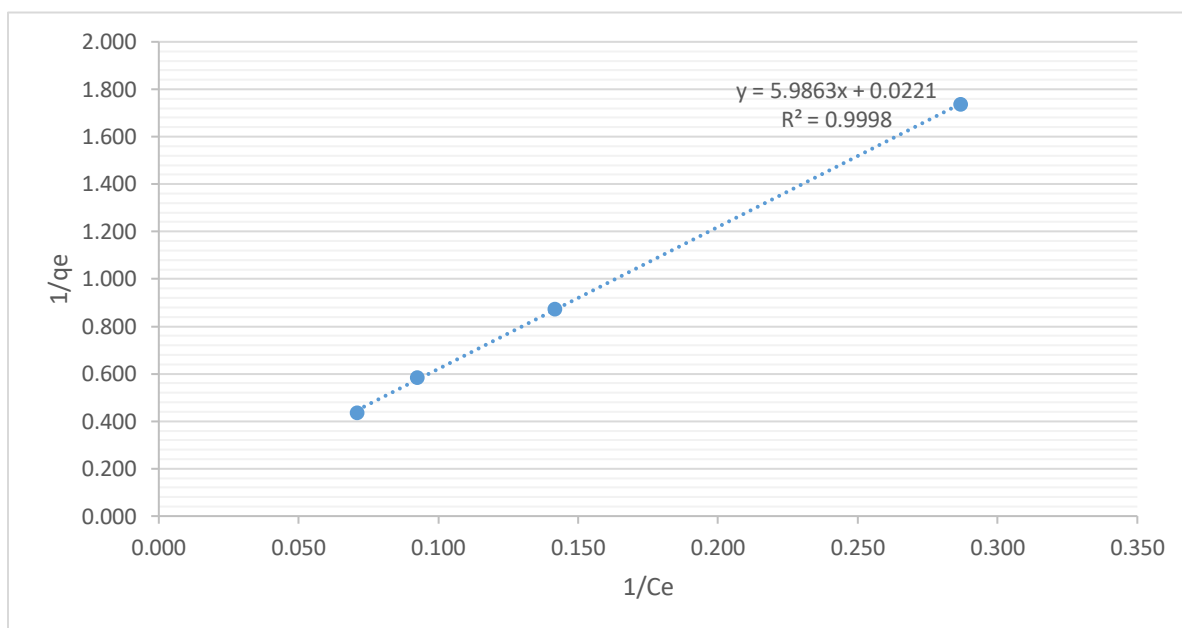


Figure (4.19): Plot of $1/q_e$ versus $1/C_e$ for chlorfenapyr in soil (2) (Abur)

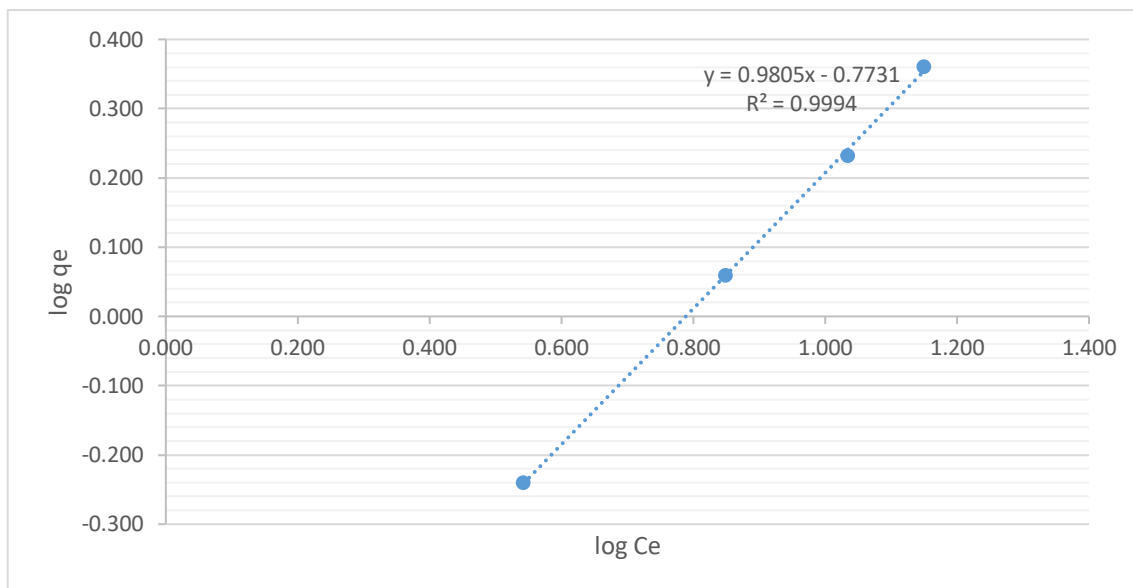


Figure (4.20): Plot of log q_e versus log C_e for chlorfenapyr in soil (2) (Abur)

The equilibrium adsorption isotherms values for cypermethrin and chlorfenapyr concentrations occurred in soil (1) and soil (2) are in (Table 4.17) and (4.18).

Table (4.17): adsorption isotherms parameters for cypermethrin

Type of soil	Langmuir				Freundlich			
	q_m (mg/g)	K_L (L/mg)	MSE	R^2	K_f (mg/g/(L/mg) ^{1/n})	n	MSE	R^2
Soil (1)	8.881	0.0123	2.23E-06	0.9999	4.031	1.52	0.0002	0.9940
Soil (2)	9.083	0.0157	2.91E-06	0.9999	2.983	1.61	0.0004	0.9875

Table (4.18): adsorption isotherms parameters for chlorfenapyr

	Langmuir				Freundlich			
Type of soil	q_m (mg/g)	K_L (L/mg)	MSE	R^2	K_f (mg/g/(L/mg) ^{1/n})	n	MSE	R^2
Soil (1)	36.232	0.0029	0.0003	0.9992	9.217	1.01	0.0001	0.9975
Soil (2)	45.248	0.0036	5.35E-05	0.9998	5.930	1.01	2.87E-05	0.9994

Adsorption tends to have n between 1 and 10. Larger value of n implies stronger interaction between the soil and the pesticides (Öztürk et al., 2004).

The n values were 1.52 and 1.61 for soil (1) and soil (2) respectively in cypermethrin, but 1.01 for soil (1) and 1.02 for soil (2) in chlorfenapyr, showing that adsorption process was favorable.

Freundlich capacity factor of both pesticides (K_F) is higher than one which shows the good interaction between the soil and the pesticides with more interaction in chlorfenapyr than cypermethrin.

For cypermethrin, K_F values were close to those reported by Layla et al. (2015). They reported that the K_F values ranged between 9.204-46.374 ml/g in soil samples. In other study, Singh and Ritu Singh (2004) reported cypermethrin K_F values of 9.12 and in soils with 0.75 and 2.16 %OC values respectively, very close to the %OM values of study site of 1.77 and 2.02. The values of K_F for chlorfenapyr on soil samples were 469.87, 550.94 and 607.16, respectively (Sun Xiao-yan et al., 2013).

The maximum adsorption capacity of cypermethrin is 8.881 mg/g and 9.083 mg/g for soil (1) and soil (2) respectively, otherwise 36.2318 mg/g and 45.2488 mg/g for chlorfenapyr in soil (1) and soil (2) respectively, which indicates a good adsorption.

The hydrophobic characteristic of cypermethrin and chlorfenapyr is the driving force for the molecule to escape to the interfaces between solvent and adsorbent surface because hydrophobic compounds are energetically favorable to accumulate at a soil - water interface rather than to remain in water.

From the results we can see that the adsorption of soil (2) was higher than in soil (1), This is due to the higher organic matter in soil (2) than in soil (1), Neururer, (1972) reported that leaching of pesticides to groundwater decreases as the soil organic matter increase, due to the decrease of the exchange capacity of soil. Also since the solubility of cypermethrin and chlorfenapyr in water is very low, this increase the adsorption process.

Also, we can see from results that the adsorption of chlorfenapyr in the two soil samples was higher than that for cypermethrin, because as the molar mass of compound increase the adsorption decrease. Hydrophilic, low molar mass compounds are more water soluble and therefore expected to be more mobile in soils and groundwater aquifers (E. A. Ghabbour and G. Davies, 2001).

Since, the correlation coefficient (R^2) values for the Langmuir isotherm are higher than that of Freundlich isotherm, and the MSE values for the Langmuir isotherm is smaller than that for Freundlich isotherm, it is clear that, the adsorption of cypermethrin and chlorfenapyr in the two soils follow Langmuir isotherm.

Although, the soil is a heterogeneous material, the adsorption data followed Langmuir isotherm, which is the representation of a monolayer, homogeneous/uniform adsorption. This may be due to the lower concentration of adsorbate in the solution, which was not sufficient to have a competition for the abundantly available adsorption sites in soil.

4.3 Potential leaching of cypermethrin and chlorfenapyr to groundwater

The Soil Adsorption Coefficient (K_{oc}) provides a measure of the ability of a chemical to sorb (adhere) to the organic portion of soil. Like K_{ow} , K_{oc} is often expressed as a log due to the wide range of measured K_{oc} values. K_{oc} indicates the potential for the chemical to leach through soil and be introduced into groundwater and partition between water and the suspended solids and sediment in the water column. Strong adsorption to soil will impact other fate properties. The adsorption classifications based on Log K_{oc} are given in Table (4.19) (USEPA, 2012).

Table (4.19): adsorption classifications based on the value of Log K_{oc}

Log K_{oc}	Adsorption Classifications
> 4.5	Very strong sorption to soil / sediment, negligible migration to ground water
3.5 - 4.4	Strong sorption to soil / sediment, negligible to slow migration to ground water
2.5 - 3.4	Moderate sorption to soil / sediment, slow migration to ground water
1.5 - 2.4	Low sorption to soil / sediment, moderate migration to ground water
< 1.5	Negligible sorption to soil / sediment, rapid migration to ground water

4.3.1 K_{oc} calculations based on soil-water partitioning coefficient K_d (L/Kg)

soil-water partitioning coefficient (K_d) measures the amount of chemical substance adsorbed onto soil per amount of water.

K_d = Concentration of chemical in soil/Concentration of chemical substance in water

$$K_d = (q_e/C_e) \times 1000$$

Values for K_d vary greatly because the organic content of soil is not considered in the equation. Since adsorption occurs predominantly by partition into the soil organic matter, it is more useful to express the distribution coefficient in K_{oc} .

K_{oc} is calculated using the following formula: $K_{oc} = K_d / \%OC \times 100$ and expressed as Liters per Kilogram of soil. K_d (partitioning between the solid-phase (soil or sediment) and solution-phase (water) at equilibrium) is normalized by multiplying the percent organic carbon content of the soil by 100.

The results of K_{oc} based on K_d for cypermethrin and chlorfenapyr for both soil sample are given in Table (4.20).

Table (4.20): The values of K_d , K_{oc} and Log K_{oc} for cypermethrin and chlorfenapyr for both soil samples

Cypermethrin	K_d	K_{oc}	Log K_{oc}
Soil (1)	67.37	3806.3	3.58
Soil (2)	84.69	4193.0	3.62
Chlorfenpyr	K_d	K_{oc}	Log K_{oc}
Soil (1)	104.40	5898.5	3.77
Soil (2)	161.99	8019.4	3.90

From the results we can see that the range of Log K_{oc} between 3.5 - 4.4 which mean that the pesticides are strongly adsorbed to soil and slow to negligible leaching to groundwater.

4.3.2 K_{oc} calculations based on Freundlich adsorption capacity K_F

$$K_{oc} = (K_F \times 100) / \%OC$$

The results of K_{oc} based on K_d for cypermethrin and chlorfenapyr for both soil sample are given in Table (4.21).

Table (4.21): The values of K_F , K_{oc} and Log K_{oc} for cypermethrin and chlorfenapyr for both soil samples

Cypermethrin	K_F	K_{oc}	Log K_{oc}
Soil (1)	4.031	227.74	2.36
Soil (2)	2.983	147.67	2.17
Chlorfenpyr	K_F	K_{oc}	Log K_{oc}
Soil (1)	9.217	520.73	2.72
Soil (2)	5.931	293.61	2.47

Since the adsorption of cypermethrin and chlorfenapyr in soil samples follow Langmuir model, this method did not give accurate results.

4.3.3 K_{oc} calculations based on octanol-water partition coefficient K_{ow}

Karickhoff (1981) and Schwarzenbach and Westall (1981) have published useful empirical equations for predicting K_{oc} as a function of K_{ow} :

$$K_{oc} = 0.411 K_{ow} \quad (\text{Karickhoff})$$

$$\text{Log } K_{oc} = 0.72 \text{ Log } K_{ow} + 0.49 \quad (\text{Schwarzenbach and Westall})$$

From Table (2.1) the values of K_{ow} for cypermethrin and chlorfenapyr are: (3.98×10^6 and 1.91×10^5) respectively, so Log K_{ow} are: (6.60 and 5.28) respectively.

The results of K_{oc} based on K_{ow} for cypermethrin and chlorfenapyr for both soil sample are given in Table (4.22).

Table (4.22): The values of Log K_{oc} based on Log K_{ow} for cypermethrin and chlorfenapyr for both soil samples

Methods used to determine Log K_{oc}	Cypermethrin	Chlorfenapyr
Log K_{oc} (Karickhoff)	6.21	4.89
Log K_{oc} (Schwarzenbach)	5.24	4.29

From the results we can see that the values of Log K_{oc} are > 4.5 which mean that the adsorption of pesticides on soil samples are very strong and the potential leaching of these pesticides to groundwater is negligible (USEPA, 2012).

All the results above from the removal percentage, kinetic and equilibrium adsorption, the physical properties of cypermethrin and chlorfenapyr and the values of K_{oc} indicate that the adsorption of these pesticides in the two soil samples is very good, which mean that the potential leaching of cypermethrin and chlorfenapyr in groundwater is very low.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The present study suggests that the kinetic adsorption of cypermethrin and chlorfenapyr on soil follows the second order kinetic model and the rate limiting step may be chemical adsorption, while equilibrium adsorption follows Langmuir isotherm describing the homogeneous, uniform and monolayer adsorption over the heterogeneous surface.

From the study it was concluded that the adsorption of cypermethrin and chlorfenapyr in soil were dependent upon physicochemical properties of soil and pesticides. In basic soils with high adsorption, the potential leaching of cypermethrin and chlorfenapyr to groundwater is very low.

5.2 Recommendations

To prevent pesticide getting to groundwater, its recommended to:

- 1- Determine the soil type and its susceptibility to leaching before using pesticides.
- 2- Choose pesticides with low susceptibility to leaching.
- 3- Follow the storage, use, and disposal directions on the pesticide label.
- 4- Properly dispose of any leftover pesticides.
- 5- Store pesticides safely, in the original labeled container and in a cool location.
- 6- Maintain records of pesticide use to avoid overuse and to help plan future applications.
- 7- Delay irrigation at least one or two days after pesticide applications.
- 8- Wherever possible, use Integrated Pest Management.

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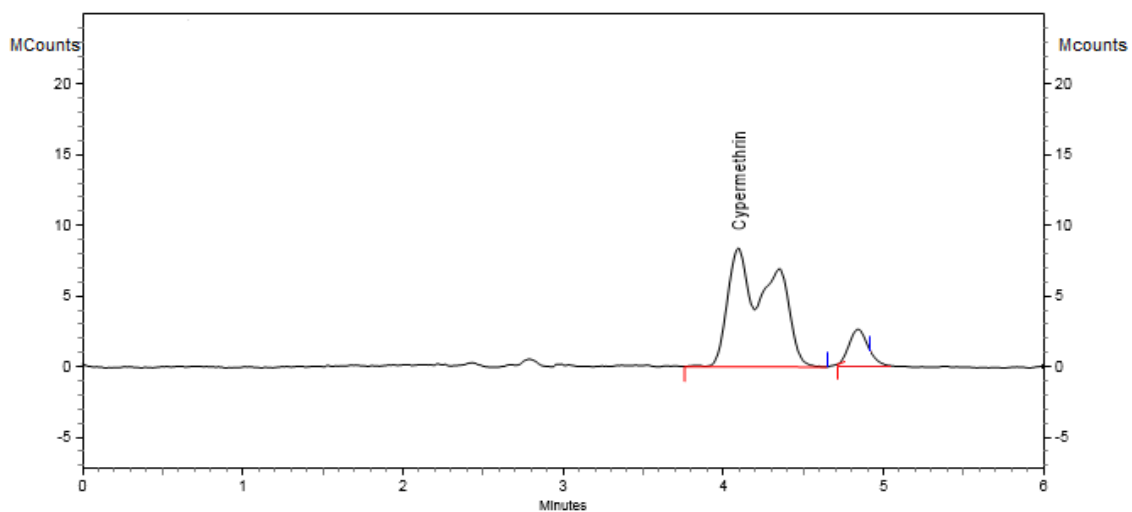
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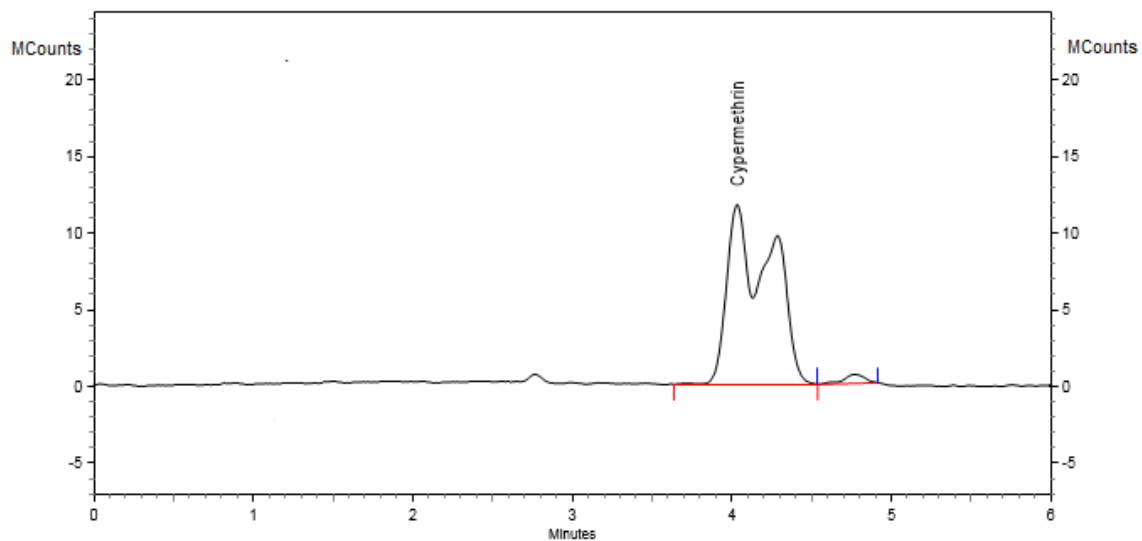
APPENDICES

APPENDIX 1

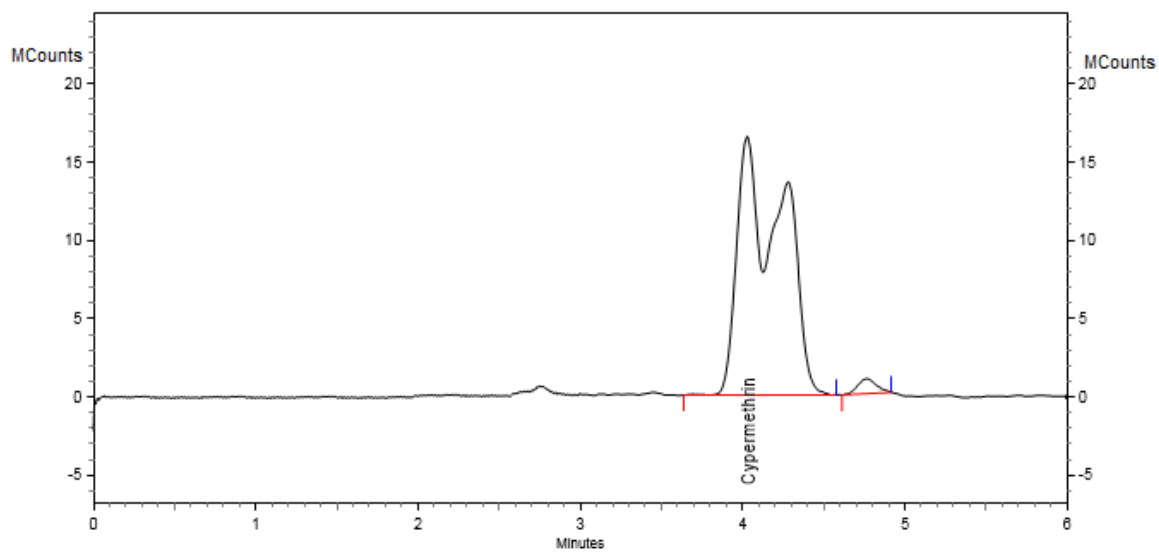
Cypermethrin calibration curve chromatograms



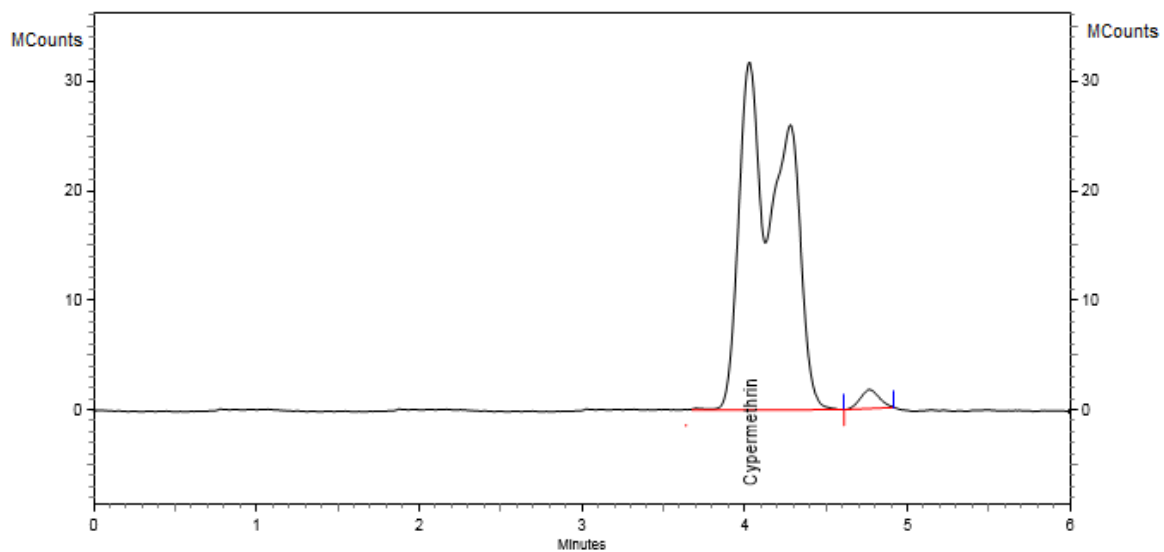
Results				
<u>Pk #</u>	<u>Name</u>	<u>Retention Time</u>	<u>Area</u>	<u>Concentration</u>
1	Cypermethrin	4.093	644494	10.000 CAL



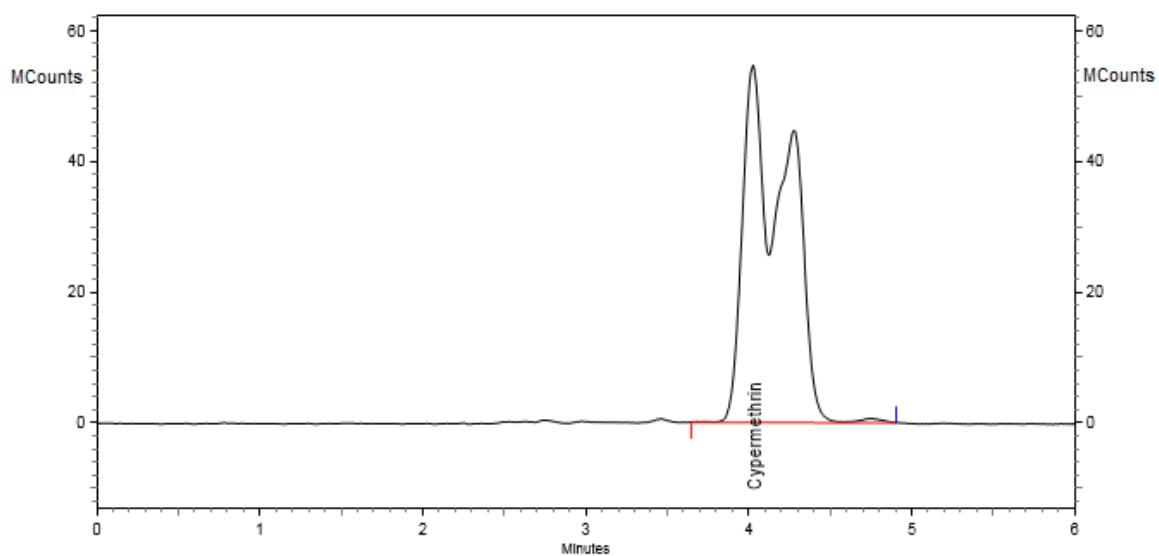
Results				
<u>Pk #</u>	<u>Name</u>	<u>Retention Time</u>	<u>Area</u>	<u>Concentration</u>
1	Cypermethrin	4.033	887250	25.000 CAL



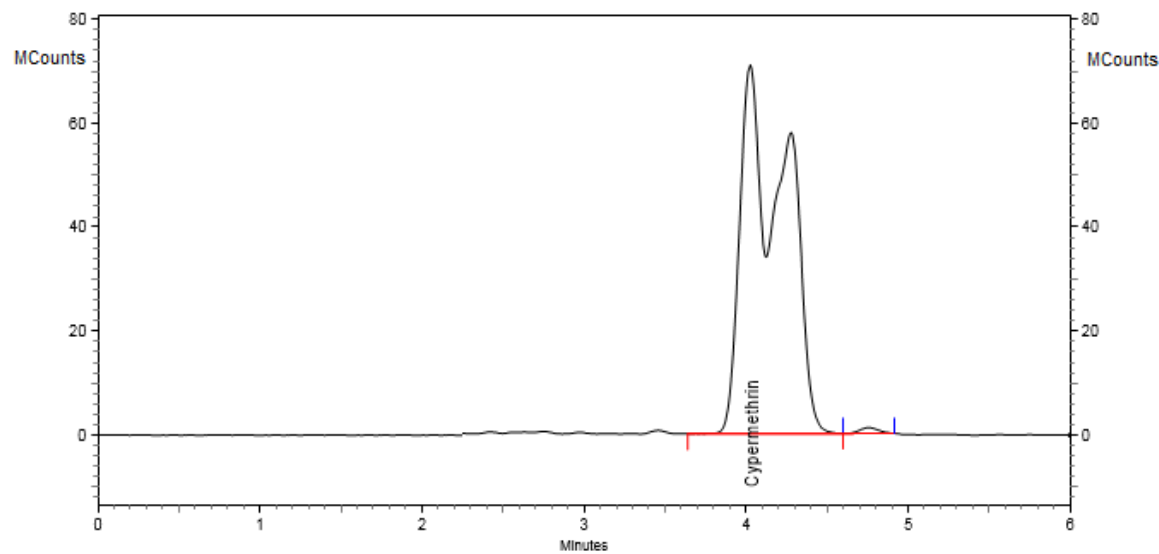
Results				
<u>Pk #</u>	<u>Name</u>	<u>Retention Time</u>	<u>Area</u>	<u>Concentration</u>
1	Cypermethrin	4.027	1345092	50.000 CAL



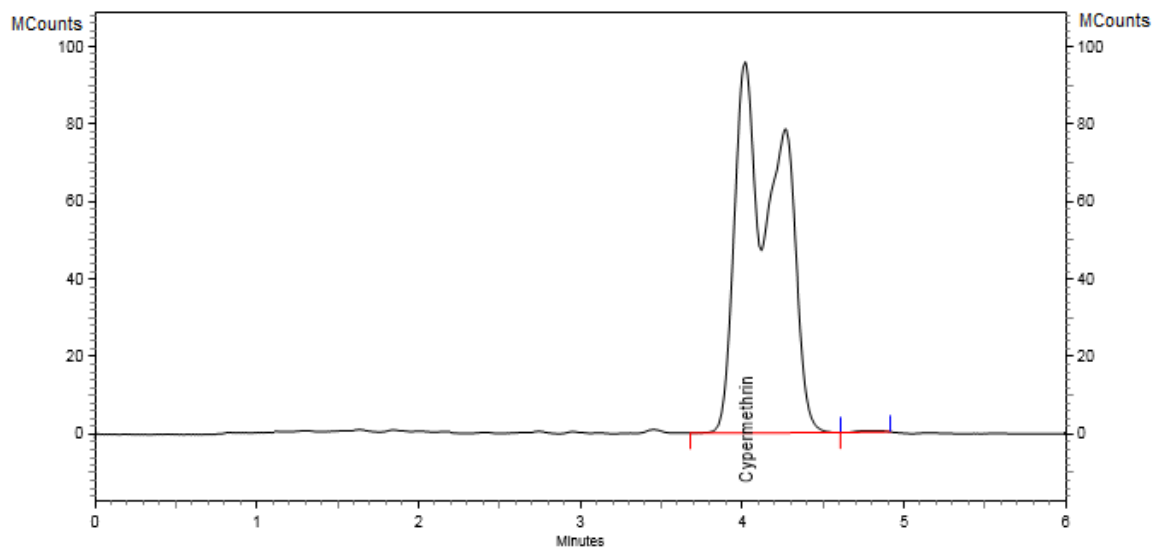
Results				
<u>Pk #</u>	<u>Name</u>	<u>Retention Time</u>	<u>Area</u>	<u>Concentration</u>
1	Cypermethrin	4.027	2693134	100.000 CAL



Results				
<u>Pk #</u>	<u>Name</u>	<u>Retention Time</u>	<u>Area</u>	<u>Concentration</u>
1	Cypermethrin	4.027	4102496	150.000 CAL



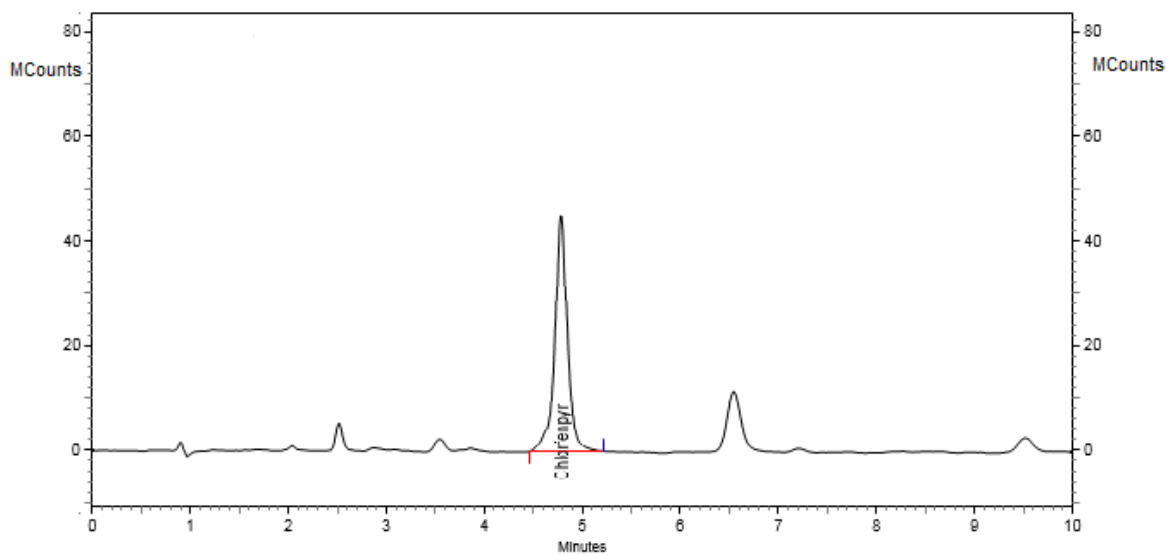
Results				
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1	Cypermethrin	4.027	5438004	200.000 CAL



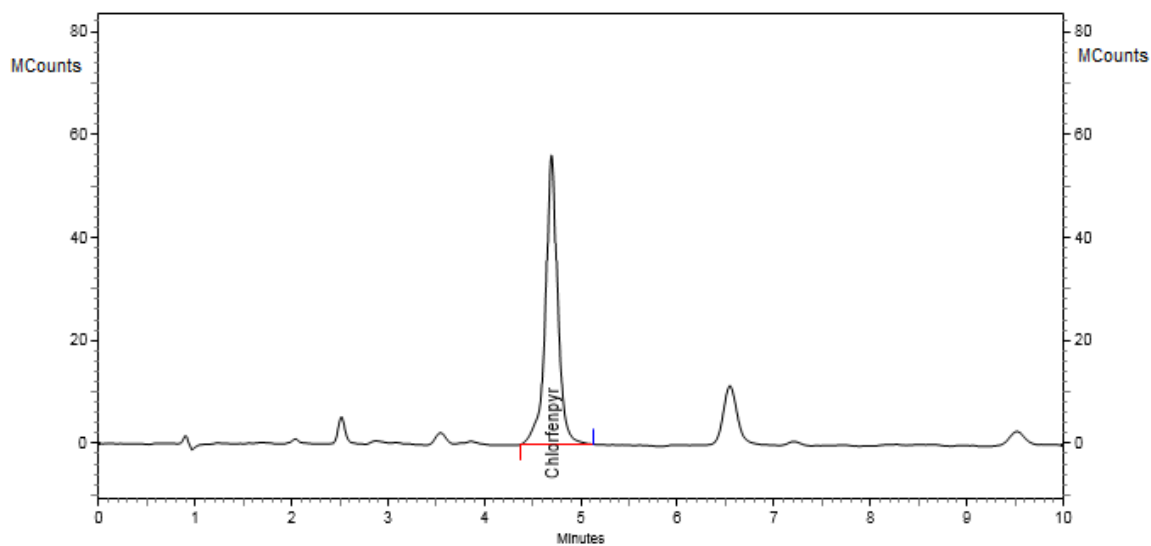
Results				
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1	Cypermethrin	4.020	7158979	250.000 CAL

APPENDIX 2

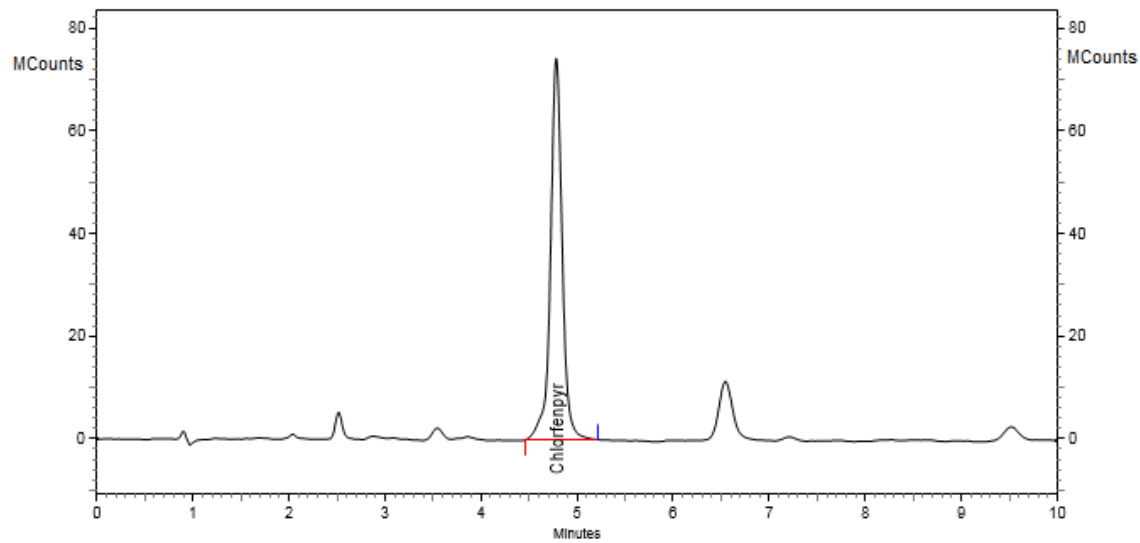
Chlorfenapyr calibration curve chromatograms



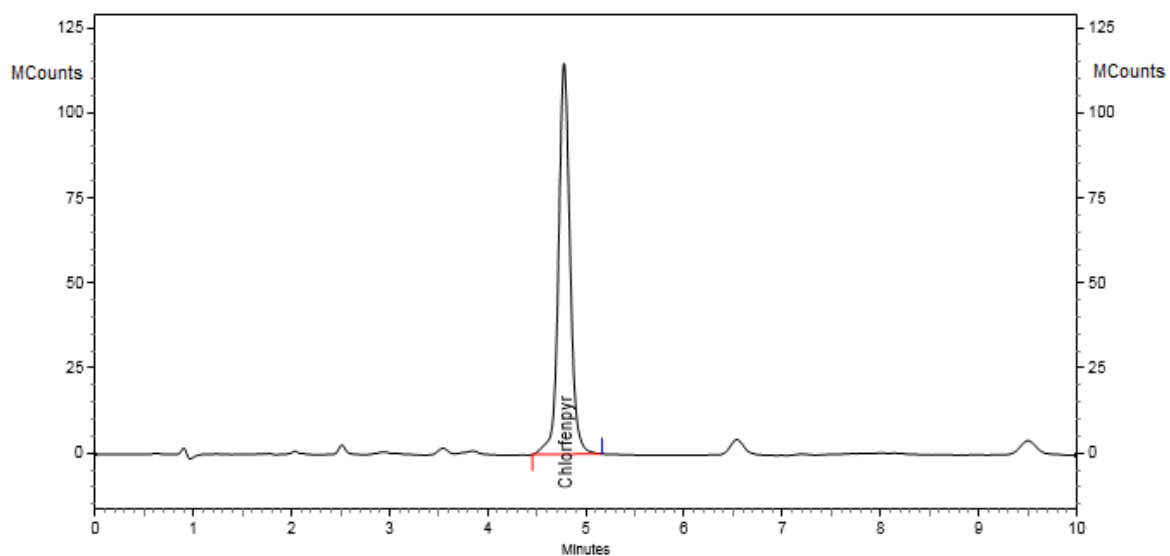
Results				
Pk #	Name	Retention Time	Area	ESTD concentration
1	Chlorfenapyr	4.780	629459	2.5 CAL



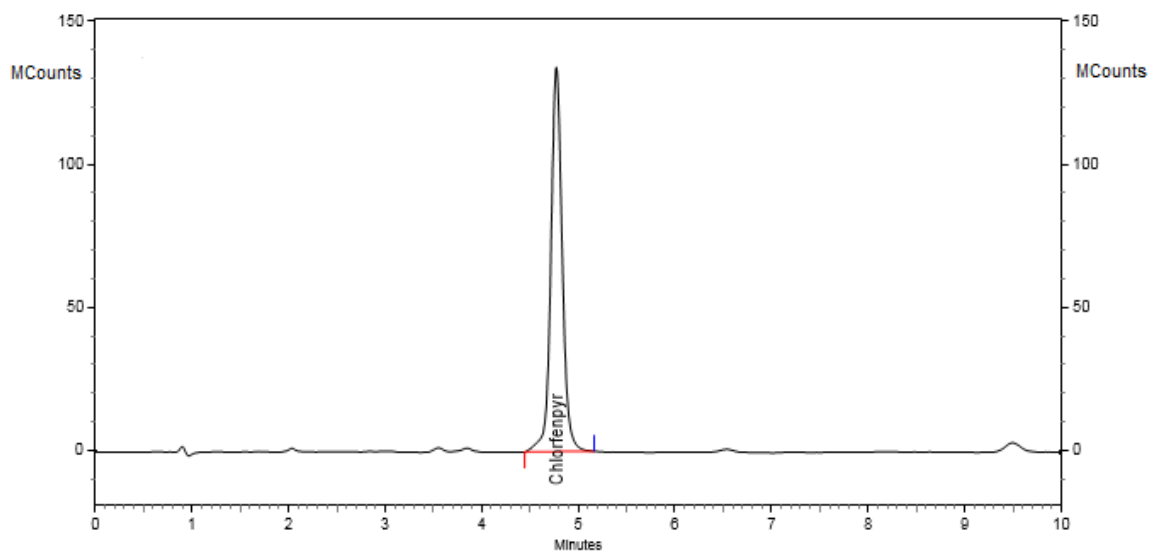
<i>Pk #</i>	<i>Name</i>	<i>Retention Time</i>	<i>Area</i>	<i>ESTD concentration</i>
1	Chlorfenpyr	4.780	1258918	5.0 CAL



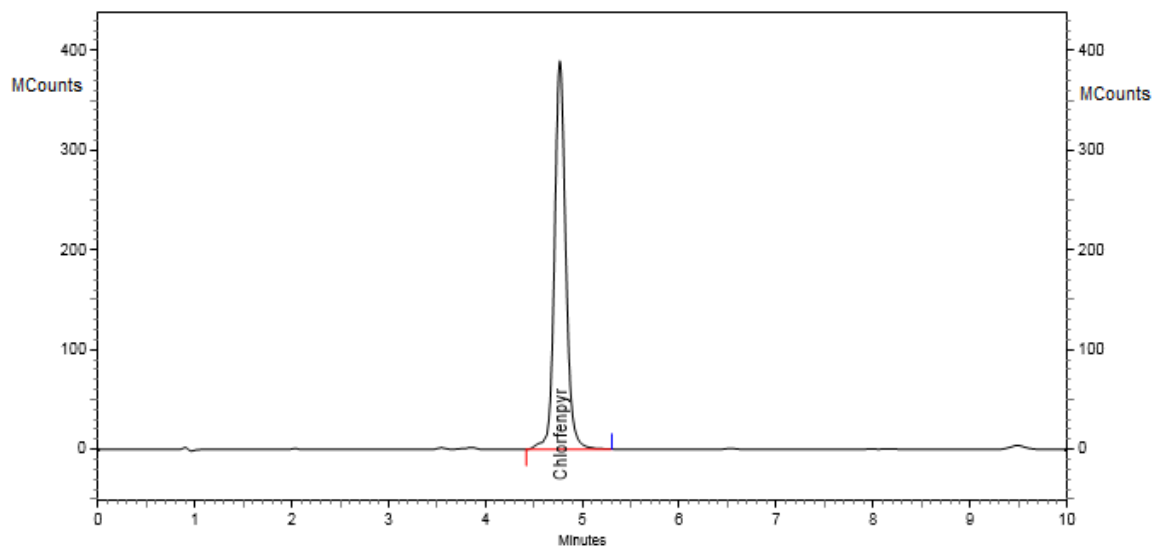
<i>Pk #</i>	<i>Name</i>	<i>Retention Time</i>	<i>Area</i>	<i>ESTD concentration</i>
1	Chlorfenpyr	4.780	2517837	10.0 CAL



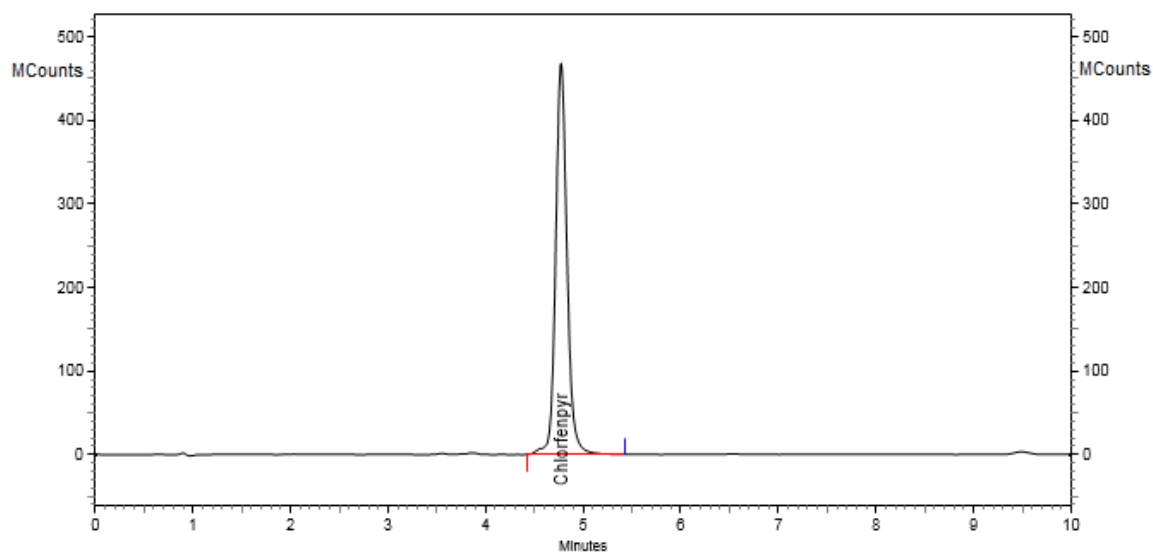
<i>Pk #</i>	<i>Name</i>	<i>Retention Time</i>	<i>Area</i>	<i>ESTD concentration</i>
1	Chlorfenpyr	4.780	4962529	20.0 CAL



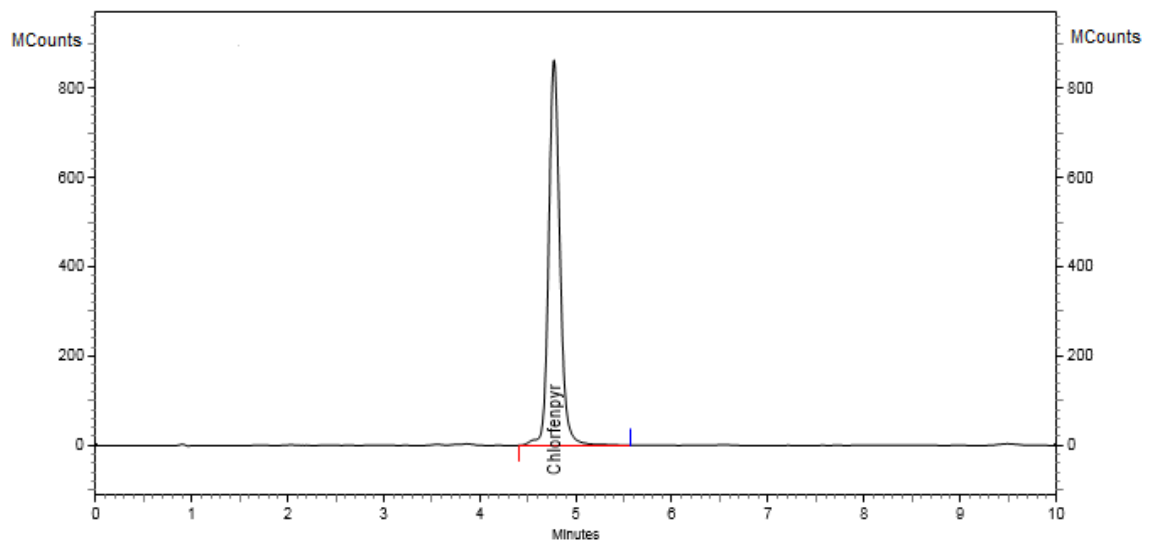
<i>Pk #</i>	<i>Name</i>	<i>Retention Time</i>	<i>Area</i>	<i>ESTD concentration</i>
1	Chlorfenpyr	4.773	8098495	30.0 CAL



<u>Pk #</u>	Name	Retention Time	Area	ESTD concentration
1	Chlorfenpyr	4.767	11612242	40.0 CAL



<u>Pk #</u>	Name	Retention Time	Area	ESTD concentration
1	Chlorfenpyr	4.773	18228473	60.0 CAL



<i>Pk #</i>	<i>Name</i>	<i>Retention Time</i>	<i>Area</i>	<i>ESTD concentration</i>
1	Chlorfenpyr	4.773	25102050	80.0 CAL

ادمصاص وإمكانية رشح المبيدات الحشرية في عينات التربة في الأردن

إعداد

احترام حازم عبدالله العوران

المشرف

الدكتور بشار محمد الصمادي

الملخص

في هذه الاطروحة تم دراسة خاصية الادمصاص لنوعين من المبيدات الحشرية في عينات التربة باستخدام طريقى المفاعل الدفعي. تم اختيار موقعين بعمق (0-30) سم في الطفيلة - الأردن لهذه الدراسة. وقد أجريت تجارب أولية لتحديد خصائص التربة، مما تبين أن نسيج العينتان كان رمليا. وكان محتوى المادة العضوية 1.77% للتربة (1) و 2.02% للتربة (2).

تم تقسيم دراسة خاصية الادمصاص إلى قسمين حركية واتزانية. وقد تم تقييم البيانات الحركية من خلال نماذج pseudo الأولى والثانية. وقد وجد أن الادمصاص الحركي لسيبرمثرين و كلورفينابير على عينات التربة يتبع pseudo الترتيب الثاني مع قيم ثابتة (1.009 غم/ ملغم.ساعة : سيبرمثرين، 11.378 غم/ ملغم.ساعة: كلورفينابير) للتربة (1) و (2.032 غم/ ملغم.ساعة: سيبرمثرين ، 13.032 غم/ ملغم.ساعة: كلورفينابير) للتربة (2).

استخدمت نماذج التماثل الحراري لانجموير و فريوندليتش لشرح ادمصاص التوازن، من هذه النماذج تم تقييم أن نموذج لانجموير أعطى نتائج أكثر دقة من النموذج الآخر مع الحد الأقصى من قدرات الامتصاص (9.083 ملغم / غم: سيبرمثرين، 36.231 ملغم / غم: كلورفينابير) للتربة (1) و (8.881 ملغم / غم: سيبرمثرين، 45.248 ملغم / غم: كلورفينابير) للتربة (2).

قيم معامل ادمصاص التربة ($\log K_{oc}$) لسيبرمثرين و كلورفينابير تتراوح ما بين (3.5-4.5) مما يدل على وجود ادمصاص قوي للتربة وعملية الترشيح إلى المياه الجوفية شبه معدومة. لذا ، فإن احتمالية رشح السيبرمثرين والكلورفينابير على المياه الجوفية منخفض للغاية ؛ بسبب عينات التربة الجيدة والخصائص الفيزيائية للمبيدات.