

**AN-Najah National University
Faculty of Graduate Studies**

**Adsorption and Desorption Characteristics of
Endosulfan Pesticide in Three soils in Palestine**

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This Thesis was defended successfully on 31/3/2009 and approved by

Committee Members

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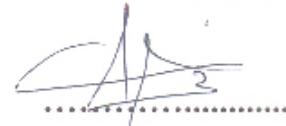
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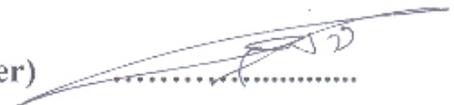
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Dedication

TO

**MY DEAR FATHER AND MOTHER FOR THEIR
SUPPORT, TO MY BROTHERS AND SISTERS, AND
TO MY HUSBAND, WITH MY LOVE AND RESPECT.**

ACKNOWLEDGMENT

Praise be to Allah, the most merciful, the most graceful for granting me the power and courage to finish this work.

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Karbalaa` Muhammad Aref Jaradat

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Adsorption and Desorption Characteristics of Endosulfan Pesticide in Three soils in Palestine

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

Declaration

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:

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Date:

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Abstract

In this thesis adsorption and desorption features were studied in details in three samples from the soil of Palestine. Soil samples were red soil, chalk soil, and sandy soil according to American Society for Testing and Materials (ASTM) scale for the classification of the soil. Adsorption and desorption rates on soil samples were calculated from kinetic studies. The values varied based on the type of soil.

Maximum specific adsorption capacities (q_{max}) for soil samples using Langmuir model, were as follows: 0,387 (red soil), and 0,281 (chalk soil), and (0.075) sandy soil mg / g of endosulfan.

Maximum adsorption was measured in red soil followed by chalk soil, but it was the least for the sandy soil. Also, the proportion of organic matter play a major role in both processes adsorption and desorption on soil samples.

here was a significant reduction in the process of Adsorption in soil samples compared with the decline in pH. Desorption was higher at both acidic and alkaline pH ranges compared to neutral pH. Both the increase in temperature and concentration increase the adsorption and desorption in all soil samples.

Finally, the results showed that the mobility of endosulfan, is more possible in the sandy soil followed by red, followed by chalk soil This may be attributed to the crystal lattice of red soil that play an important role in both processes adsorption and desorption, as it could be a major role for chemical and biological processes that play a role in the other soil samples.

CHAPTER ONE
INTRODUCTION

1.1 INTRODUCTION

Persistent Organic Pollutants (POPs) are a set of chemicals that are toxic, persist in the environment for long periods of time, and biomagnify as they move up through the food chain . POPs have been linked to adverse effects on human health and animals, such as cancer, damage to the nervous, reproductive disorders, and disruption of the immune system. Because they circulate globally via the atmosphere, oceans, and other pathways. POPs released in one part of the world can travel to regions far from their source of origin (Sandra et al. 2006).

With mounting evidence, indicating the long-range transport potential of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment, the international community has called for urgent global actions to reduce and eliminate their release into the environment (Burger et al., 2001).

Organochlorines (OCs), represent an important group of POPs which have caused worldwide concern as toxic environmental contaminants (Law et al. 2003, Covacia et al., 2005) and (Wurl and Obbard, 2005).

The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and the subsequent magnification of concentrations in organisms, progressing through to the food chain (Tanabe, 2002 and Helberg et al. 2005). Specifically, one of the key

environmental concerns, regarding some POPs, is their occurrence in Polar Regions, at surprisingly high levels.

Organochlorine pesticides (OCPs) are still widely distributed in the environment due to their persistency, semi-volatile nature resulting in long-distance transportation (Zhang H.B et al. 2006).

Accumulation of OCPs also in the lipid content of animals is a common phenomenon due to their hydrophobic properties (Sijm and linde, 1995). Investigation of sorption phenomena of pesticides in soils is of great importance from environmental point of view. Pesticide sorption affects other processes like transport, degradation, volatilization, bioaccumulation, which influence the final fate of these compounds in the soil environment (Gao et al., 1998). All these processes influence the extent of surface water and ground water contaminations. Moreover, soils are a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying composition and surface activity. They can bind pesticides and reduce the bioavailability (Torrents and Jayasundera, 1997). Thus, knowledge of the pesticide adsorption–desorption characteristics of soil is necessary for predicting their mobility and fate in soil environments and also to understand whether bioremediation is a feasible option for the clean up of contaminated soil.

Numerous studies have been reported about the strong relationship between total organic carbon in the soil and the mobility of pesticides.

In this study, we focused on studying adsorption and desorption characteristics of endosulfan on various soils though they are of fundamental importance to quantify the transport of pesticides and the selection of proper remediation technique. The importance of organic matter, particle size, as well as pH of the soil for sorption has been emphasized by many workers (Huang and Mckercher, 1984, Barriuso et al., 1992 and Gao et al., 1998). These factors however, have not been studied in details for endosulfan, which is used widely in agriculture in

Palestine. Therefore, investigation of these processes will provide a better understanding of its sorption and transport in soil environments.

1.2 Pesticide history and Classification

A pesticide is a substance or a mixture of substances used for preventing, controlling, or lessening the damage caused by a pest (Parads, G. et al., 1995). A pesticide may be a chemical substance, biological agent (such as a virus or bacteria), antimicrobial, disinfectant or device used against any pest. (USEPA, 2007).

Pesticides are used to control organisms which are considered harmful. (Purdue.edu, 2007). Pesticides can save farmers money by preventing crop losses to insects and other pests; in the US, farmers get an estimated four-fold return on money they spend on pesticides (Kollogg RL, et. al, 2000). One study found that not using pesticides reduced crop yields by about 10%. (Kuniuki S, 2001).

The first recorded use of pesticide to protect crops was 4,500 years ago (Miller, GT. 2002). In 1993 Paul Muler discovered that DDT was a very effective insecticide. In 1940s, manufacturers began to produce large amounts of synthetic pesticides and their use became widespread (Daily, H, et al., 1998). Pesticide use has increased 50-fold since 1950 and 2.5 million tons (2.3 million metric tons) of industrial pesticides are now used each year (Miller, G. T. 2002).

In the 1960s, it was discovered that DDT was preventing many fish-eating birds from reproducing, which was a serious 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 disease-carrying insects (Lobe, J. 2006).

1.3 Pesticides effect 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 (Kollogg, R.L., 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 (Kollogg, R. L., 2000).

1.4 Effect of pesticide on soil quality

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 used and 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 possibility causing adverse impacts on aquatic ecosystems (Jaenicke, E.C., 1998).

1.5 The fate of pesticides in the environment.

A pesticide stays in the treated area long enough to produce the desired effect and then degrades into harmless materials (Miller, 1993).

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.

The half-life is the amount of time it takes for half of the pesticide to be converted into something else, or its concentration is half of its initial level. The half-life of a pesticide depends on soil type, its formulation, and environmental conditions (e.g., temperature, moisture). If pesticides move off-site (e.g., wind drift, runoff, leaching), they are considered to be pollutants (Rosales-Conrado N. et, al.2002). The potential for pesticides to move off- site depends on the chemical properties and formulation of the pesticide, soil properties, rate and method of application, pesticide persistence, frequency and timing of rainfall or irrigation, and depth to ground water (Sparks R., 2003). These processes are summarized in figure 1.1.

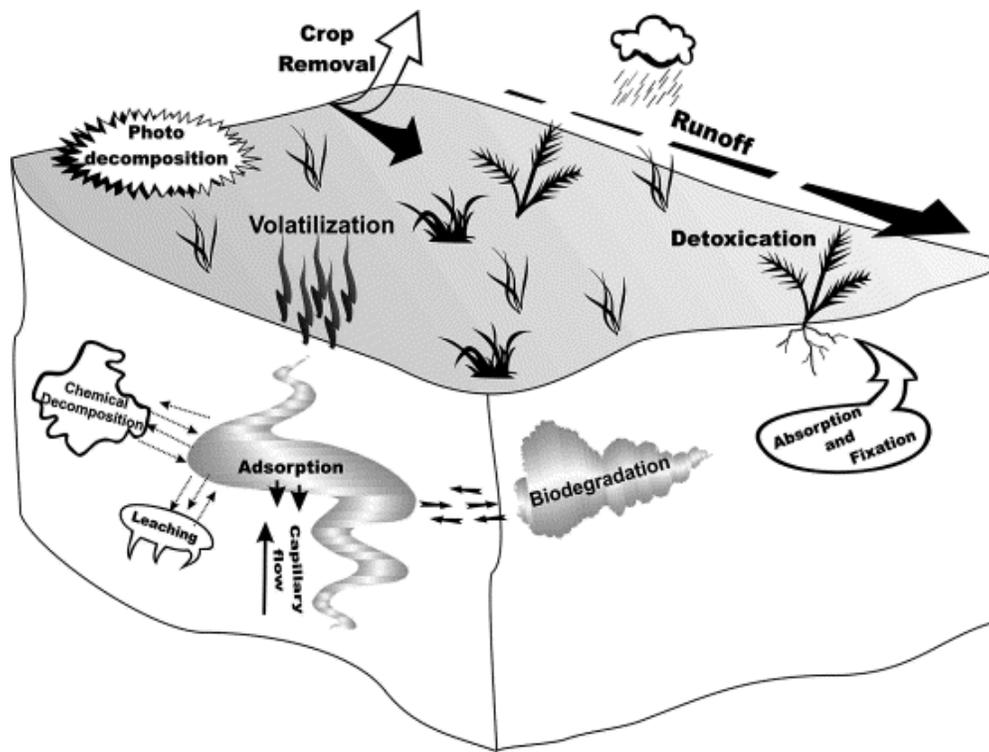


Fig. (1.1): Fate of pesticides in soil.

Whether they are destroyed over a period of few days by soil microorganisms or whether they are accumulated steadily from year to year, the fate of pesticides in soils varies greatly, depending on the type of soil, the climate and the agricultural practices used (Luque-García J.L. et al. 2002), and (Perrin-Ganier, C. et al., 2001).

1.6 Retention of pesticides in the soil

Retention refers to the ability of the soil to hold a pesticide in place and not allow it to be transported. Adsorption is the primary process of how the soil retains a pesticide and is defined as the accumulation of a pesticide on the soil particle surfaces. Pesticide adsorption to soil depends on both the chemical properties of the pesticide (i.e., water solubility, polarity) and properties of the soil (i.e., organic matter and clay contents, pH, surface charge characteristics, permeability). For most pesticides, organic matter is the most important soil property controlling the degree of adsorption. For most pesticides, the degree of adsorption is described by an adsorption distribution coefficient (K_d), which is mathematically defined as the amount of pesticide in soil solution divided by the amount adsorbed to the soil (McBride, 1994) .

1.7 Pesticides usage in palestine

Pesticides are being used in all parts of the Palestinian Districts for various purposes. They are used in households, public health, the veterinary sector, and in the agricultural sector.

Plant diseases and pests are considered one of the most common factors that obstacle and reduce both quantity and quality of agricultural products. Therefore, in order to produce high products with suitable quality, it is necessary to control the pests in the region of Palestinian Authority. More than 160 types of pesticides (active ingredient), herbicides, fungicides, or insecticides are used. The consumption of active ingredients from different types of pesticides are annually estimated in the region of Palestinian Authority as 1800 tons, of which 1200 tons fumigation materials mainly Methyl Bromides, and about 600 tons of various kinds of pesticides, the average of pesticides usage is about 3.3kg per dunum annually, in addition to about 6.6 kg methyl bromide per dunum Methyl Bromide (Ministry of Agriculture, 1995).

Agriculture is the backbone of the Palestinian economy, contributing 33% and 24% of the Gross National Products in the West Bank and Gaza strip, respectively (ARIJ, 1994). West Bank agriculture has, in the last few years, increased in sophistication, and this has had many negative side effects, of which the overuse of pesticides could prove to be the most serious one (WRI 1994, Igbedioh 1991).

Farmer`s use of pesticides increased, particularly in irrigated farming. Unfortunately, this increase has not been accompanied by a full understanding of the impacts of pesticides on human health, beneficial organisms and the environment (Sansour 1991, Igbedioh 1991). This attitude has been shown elsewhere to lead into a vicious cycle of ever increasing usage and ever diminishing returns (WRI 1994).

The problem is not limited to the West Bank, of course, and has afflicted all of the neighboring countries. Pesticide usage is a major area of concern in Israeli agriculture, for instance, and much effort has recently been expended to find alternatives to pesticides. While Israel has been quite successful in using biological control in citrus orchards, they are still in the experimental phase with regard to vegetable cultivation (Horashof 1991).

1.8 Types and properties of pesticides used in Palestine

A total of 408 pesticides currently being used in the West Bank are presented in tables 1-5, (Ministry of agriculture, Palestine, 2007)

Table (1.1): Herbicides used in Palestine.

Generic name	Formulator	Concentration of active ingredient	Brand Name
Terbutryne	Syngenta	500 g/L	Agrein 500
Tribenuron methyl	Dupont	75%	Express
Triasulfuron	Syngenta	75%	Amber or Logran
Terbutryne + Ametryne	Agan	25+40%	Amign 65
Sulfometuron methyl	Dupont	75%	Oust 75
Ethidimuron	Bayer	70%	Ustilan
Linuron	Agan	500g/L	Aflon
2,4-D salt	Nufarm	96.9%	Aminbar
Carfetraxone ethyl	FMC	40%	Aurora
Phenmedipham	Bayer	157g/L	Betanal
2,4-D (Tri-ethanol amine salt) Makhteshim.	chemical works Ltd	500g/L	Alber 40
2,4-D Makhteshim	chemical works Ltd.	335g/L	Albur super
Imazethapyr	BASF	100g/L	Persut
Prometryne	Agan	500g/L	Prometrex

Generic name	Formulator	Concentration of active ingredient	Brand Name
Prometryne	Sipacam	500g/L	Prometron
Prometryne	Syngenta	500g/L	Promegard
Glufosinate ammonium	Bayer	200g/L	Basta 20
Glufosinate ammonium	Tabozal	200g/L	Bastr
Benfluralin	Agan	180g/L	Benefex 18
Sulfentrazone	FMC	75%	Boral
Fenoxaprop -P-ethyl + Mefenpyr diethyl	Bayer	69+18.8 g/L	Puma super
Ammonioium thiocyanate	Agan	220g/L	Bedozol TL
Chloridazon (Pyrazon)	Basf	65%	Pyramin
Quizalofop-p-ethyl	Nissan	100g/L	Bilot soper
Glyphosate Trimesium sulfate	Syngenta	480g/L	Touchdown
Terbutryne	Agan	500g/L	Terbutrex
Aclonifen	Bayer	600g/L	Challenge
Picloram + 2,4D	Dow Agrosiences	102g/L + 396g/L	Tordon 101
Sulfometuron methyl	Generex Australia	75%	Tostar
Fluroxypyr	Agan	200g/L	Tomahawk
Flufenacet	Bayer	60%	Tarh
Rimsulfuron Methyl	Dupont	25%	Titus
Glyphosate Isopropy Amine Salt	Tabozal	480g/L	Taifun 262

Table (1.2): Fungicides used in Palestine

Generic name	Formulator	Concentration of active ingredient	Brand Name
Spiroxamine	Lied Chemical	500g/L	Impulse
Quinoxifen	Dow Agrosiences	250g/L	Abeir
Fenbuconazole	Dow Agrosiences	50g/L	Indar
Hexaconazole	Syngenta	50g/L	Anvil
Tolyfluanid	Lied chemical	50%	Aoperin Multi
Tebuconazole	Irvita	250g/L	Orios
Penconazole	Dr. Miron	100g/L	Ofir
Prochloraz	manganese Bayer	50%	Octav Or Sportak
Fluazinam	ISK Japan	500g/L	Ohaio
Triadimenol	Lied chemical	250g/L	Bayfidan
Bitertanol	Bayer	25%	Baycor
Copper hydroxide	Nufarm	77%	Parasol
Mepanipyrim	Kumiai chem.	50%	Prupica
Dazomet	Basf	98%	Bazamid
Oxycarboxin	Chemtura (Pty)	75%	Plantax
Copper hydroxide	Agri estrella	77%	Blu shield
Iminoctadine tris	Nippon soda	40 %	Blekiot
Flusilazole	Dupont	400g/L	Punch40
Difenoconazole	Dr. Merion	250g/L	Bogard
Copper Sulphate	Tabozal	80%	Bordozol
TCMTB	Buckman Lab.	300g/L	Busan
Tebuconazole	Dr. Miron	250g/L	Polyron
Carbendazim	Basf	50%	Bavistin
Quintozene (PCNB)	Chemtura	75%	Terachlor
Fenhexamid	Bayer	500g/L	Teldor
Flutolanil	Nihon nohyau	410g/L	Telem

Generic name	Formulator	Concentration of active ingredient	Brand Name
Penconazole	Glopachem	100g/L	Topnex
Tebuconazole	Indalva Quimica	45%	Tebax
Sulphur	Spyros Bioscience	70%	Gafribk
Benalaxyl + copper	oxychloride Agrimont	4% +33%	Galben copper
Flutriafol	Cheminova	125g/L	Hosan <i>or</i> Impact
Propamocarp HCL	Bayer	722g/L	Dynone <i>or</i> previcur
Carbendazim	Dupont	50%	Delsene
Dithianon	BASF	500g/L	Delan
Propamocarp HCL	Chimac Agriphar	722g/L	Dotan <i>or</i> proplant
Pyrifenox	Syngenta	200g/L	Dorado 200
Carbendazim + diethofencarb	Sumitomo	250+250g/L	Resec
Fenarimol	GOWAN	120g/L	Rubigan
Iprodione	Agriphar	500g/L	Rodion
Triforine	Sumtoma	199g/L	Saparol
Bromuconazole	Bayer	100g/L	Vectra
Trifloxystrobin	Bayer	50%	Flant

Table (1.3): Insecticides used in Palestine

Generic name	Formulator	Concentration of active ingredient	Brand Name
Triflumuron	Lied Chemical	25%	Alsystin
Buprofezin	Nihon Nohyaku	250g/L	Aplord
Clofentezine	Irvita plant protection	50g/L	Apollo
Abamectin	Syngenta	18g/L	Agremic
Thiocyclam hydrogen oxalate	Syngenta	50%	Evisect S
Indoxacarb	Dupont	150g/L	Afent
Abamectin	Burchemresearch	18g/L	Acremakten
Halfenprox	Mitsui Toatsu	50g/L	Annivers
Chlorfluazuron	ISK	50g/L	Attabron
Cyfluthrin	Lied Chemical	50g/L	Baythroid
Diafenthiuron	Syngenta	250g/L	Pegasus 25
Azocyclotin	Lied Chemical	25%	Peropal
Deltamethrin	Bayer crop science	25g/L	Becis
Bacillus	Thuringensis Valent Biosciences	8500 mg/l	Bktosfen
Abamectin	Tbaon chem	18g/L	Bakten
Polybutene	Rimi Chemical	60%	E Poly tarf
Diafenthiuron	Indalvaquimica	500g/L	Ponza
Bacillus Thuringensis	Rimi chemical	8000 mg /l	Bio . TION.

Table (1.4): Acaricides used in Palestine

Generic name	Formulator	Concentration of active ingredient	Brand Name
Methiocarb	Lied Chemical	50%	Mesurool
Tebufenpyrad	BASF	20%	Masy
Dimethyl	polysiloxanes Witco	100%	Mshtah L77
Acetamiprid	Agan	200g/L	Mosblan
Teflubenzuron	BASF	150g/L	Molit
Milbemectin	Sankyo co.	9.3g/L	Melpnok
Fenamiphos	Bayer	10%	Neemacor 10
Gossyplure	Certis	8%	Farmon
Bifenazate	Chemtura	240g/L	Flormait
Summer oil	Makhteshim chemical works Ltd	80%	Vitol OL
Abamectin	Syngenta	18g/L	Vertimec
Summer oil	Tarsis Ltd.	80%	Virotar OL
Etofenprox	Mitsui Toatsu	300g/L	Sensor
Garlic extract	Multicrop	15g/L	Som Hrk
Cypermethrin	Rimi Chemicals ltd.	100g/L	Siperin 10

Table (1.5): Other pesticides used in Palestine

Trade name	Active ingredient
Neman	Fenaminophos
Methyl Bromide	CH ₃ Br

1.9 Extent of pesticide usage in palestine

The total cultivated area of the West Bank is around 2 million dunums. Of this, only 100 thousand dunums are under irrigation, while 1.6 million dunums are rainfed and 300 thousand dunums are fallow lands (ARIJ, 1994). It is estimated that 96.6% of irrigated land and 87.0% of rainfed land is treated with pesticide.

This survey reveals an overuse of pesticides in the West Bank, particularly in irrigated areas in Tulkarem, Jenin, and Jericho. The average seasonal consumption of pesticides was found to be around 4kg/dunum in open irrigated fields and 6.5 kg/dunum under plastic, excluding usage of methyl bromide, which is measured in liters (Table 6).

Of total pesticide used, insecticides contribute 49.4%, fungicides 33.7% and herbicides 12.78%.

The total quantity of pesticide (including Methyl Bromide) used in the West Bank is estimated to be around 1800 tons per year, of which about 200 tons are methyl bromide, 72 tons are sulfur (50 tons of which are consumed in Hebron). All but 4 tons are used for agricultural purposes, the remainder being used for domestic purposes such as public health. The districts show variations in the quantity of pesticide used, because of factors such as whether the area is irrigated or not, the crops that are cultivated, the farming patterns used, topography, and climate.

Table(1.6): The average amount of pesticide and the proportion of insticide, fungicide, herbicide and others used in Palestine according to district and cropping type.

District	Cropping type	kg/dunm	Insecticides (%)	Fungicides (%)	Herbicide (%)	*Others (%)
Tulkarem	Open irrig	1.60	51.0	32.0	10.7	6.30
	Plastic	3.3	42.2	45.5	6.50	5.80
Jenin	Open irrig	2.10	48.0	26.0	25.5	0.50
	Plastic	4.00	53.0	32.8	9.0	5.20
Jericho	Open irrig	2.60	55.5	32.9	9.5	2.10
	Plastic	6.00	46.5	33.2	15.5	4.80

* Other kinds of pesticides such as: acaricides, rodenticides, molluscicides,, etc are also used.

Table (1.7): Areas treated with pesticides in districts according to crop pattern (dunums)

District	Irrigated Farming				Rainfed Farming			
	Crop pattern	Vegetables in plastic houses	Vegetables in open field	Trees	Field crops	Vegetables	Trees	Field crops
Nablus		13	1945	1500	0	1650	5535	16450
Tulkarem		5710	8021	13000	0	12000	9260	40000
Jenin		210	12000	1740	0	12000	9260	40000
Jericho		120	29995	6411	6120	0	0	22
Ramallah		20	1131	0	0	4100	37560	7000
Hebron		0	526	0	0	9630	74744	12800
Subtotal		673	53608	22651	6120	33510	168719	92772
Total			88452			295001		

As indicated by the previous table (7), the total area treated with pesticide is 383,453 dunums, 77% of which is under rainfed farming, and 23% of which is under irrigated farming. Still, irrigated farming accounts for about 72% of total pesticide consumption. This is due to the intensive nature of cropping methods used in irrigated farming: methyl bromide, for instance, which is not used in rainfed areas, constitutes around 56.3% of pesticide use in irrigated farming.

Pie charts 1 and 2 (Fig.1.2) and (Fig.1.3) present the average treated area according to district and crop pattern respectively. As Pie 1 shows, 25% of the treated area is in Tulkarem, while only 7% is in Jericho. Pie 2 shows that 44% of the total treated area in the West Bank is cultivated with rainfed trees, while a mere 2% is cultivated with plastic houses.

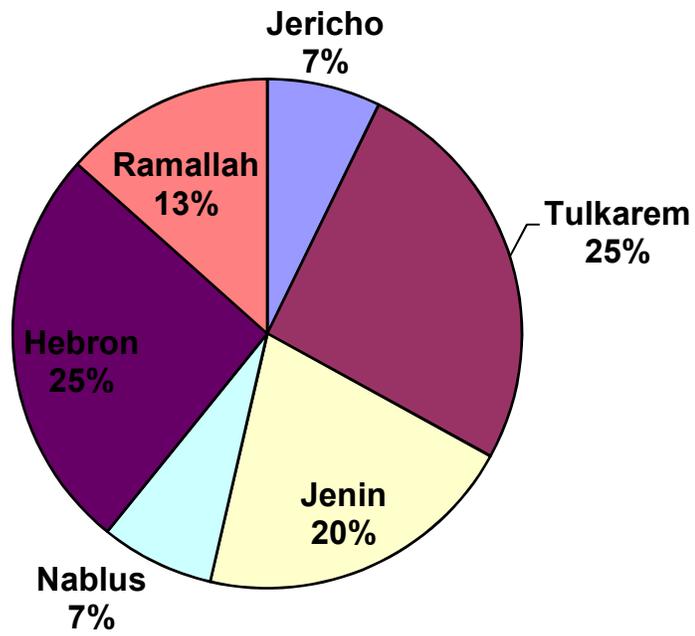


Fig. (1.2): Average Treated Area According to District

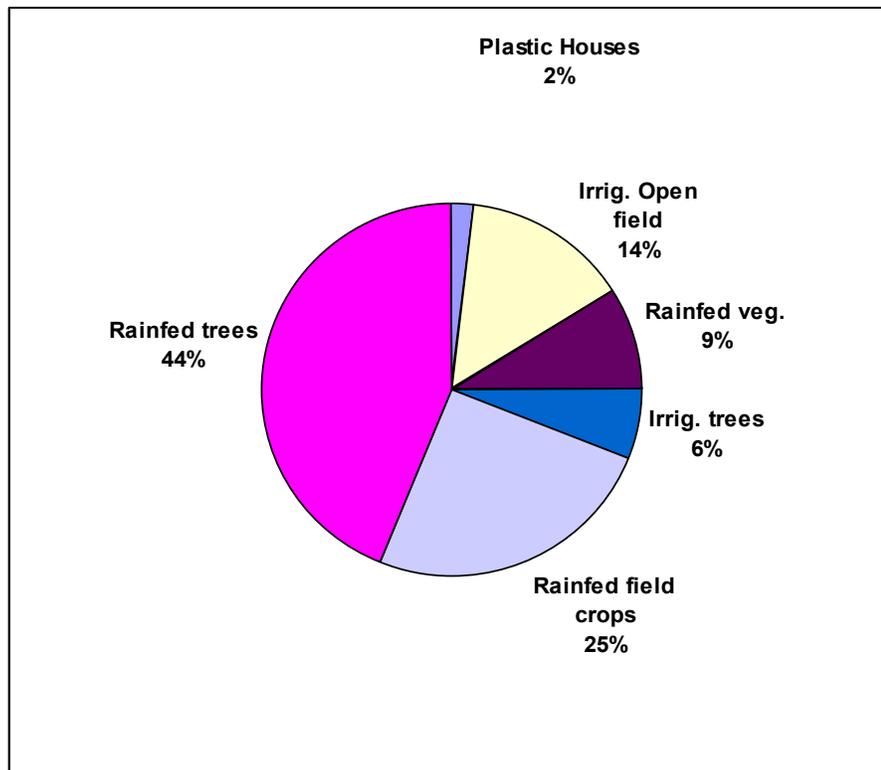


Fig (1.3): Average Treated Area According to Crop Pattern

The results of information collected are illustrated in Table 8, which shows quantities of pesticide used by district and by cropping pattern. It is clear from the table that Jericho, Tulkarem and Jenin consume about 61% of the pesticides in the West Bank. Irrigated agriculture, for which pesticides are most intensively used, is concentrated in these three regions, above all in Jericho.

Table (1.8): Quantities of pesticides used by districts according to cropping pattern

District							
Crop pattern	Nablus	Tulkarem	Jenin	Jericho	Ramallah	Hebron	Total
Irrig. Trees	0.780	9.050	1.514	2.735	0.000	0.000	14.079
Irrig. Field crops	0.000	0.004	0.000	1.281	0.000	0.000	1.285
Vegetables in plastic houses	0.084	18.843	0.840	0.720	0.130	0.000	20.617
Vegetables in open fields	2.124	12.832	25.200	77.961	0.960	0.288	119.335
Subtotal	2.978	40.731	27.554	82.697	1.090	0.266	115.316
Rainfed trees	5.958	12.262	1.986	0.000	17.867	45.407	83.480
Rainfed field crops	3.390	3.670	4.000	0.000	1.445	2.740	15.275
Rainfed vegetables	4.390	1.560	2.500	0.000	6.410	20.888	35.748
Subtotal	13.768	17.492	8.468	0.000	25.722	69.035	134.503
Total	16.476	58.223	36.040	82.697	26.812	69.301	289.819

Vegetables, especially when irrigated, clearly have the highest pesticide use, probably because of their high monetary return per dunum and the high potential of there being pest damage and consequent losses.

Pie charts 3 and 4 (Fig.s 1.4 and 1.5) show average pesticide consumption according to district and crop pattern respectively. Pie 3 clarifies that Tulkarem consumes the largest amount of pesticide, 29% of total consumption. As pie 4 shows, irrigated open field vegetables are the most pesticide consuming crop pattern, accounting for 41% of total pesticide use.

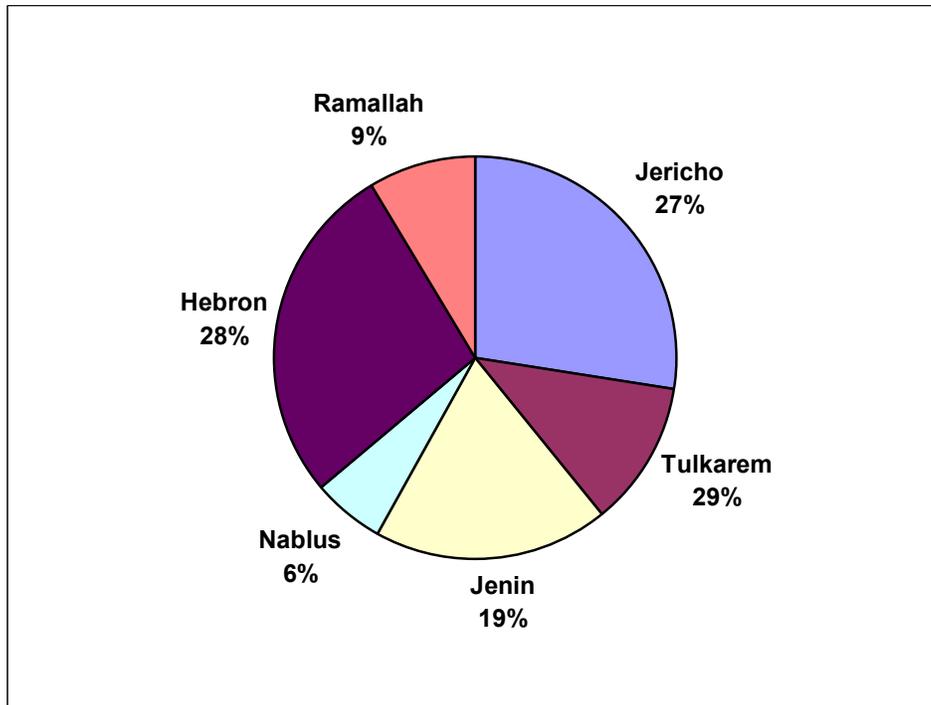


Fig .(1.4): Average Pesticide Consumption According to District

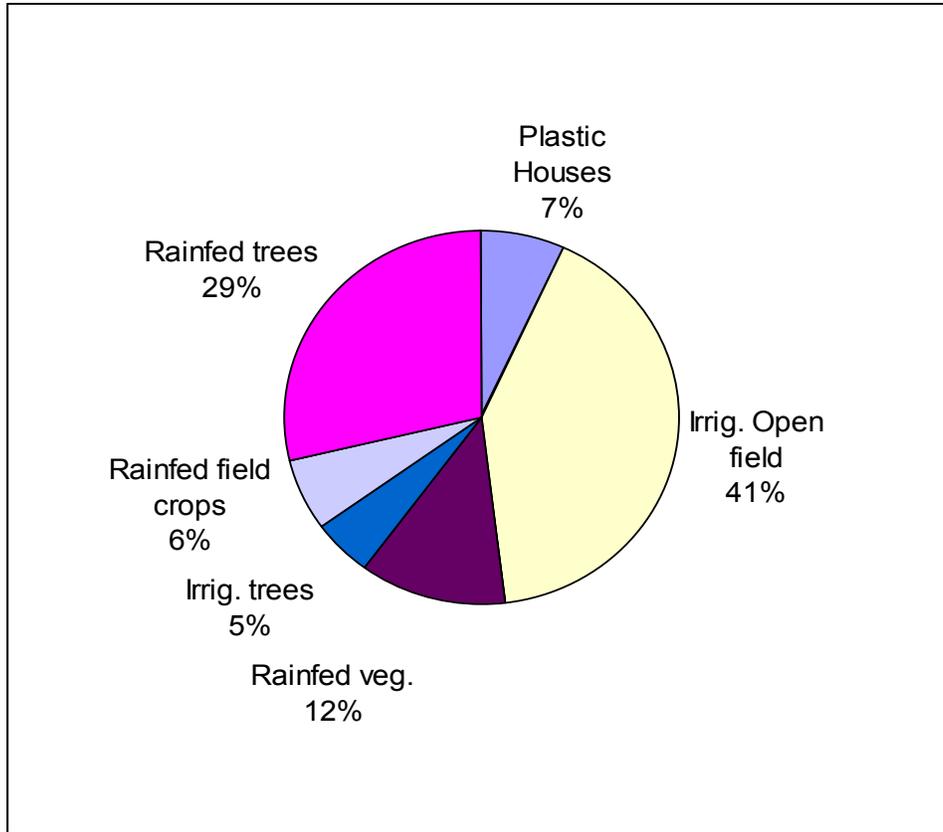


Fig . (1.5): Average Pesticide Consumption According To Crop Pattern

Methyl Bromide constitutes almost 40.5 % of total estimated pesticide use in the West Bank. It is used predominantly as a preplanting treatment (soil fumigant) against soil borne pests. Its negative effects on the ozone layer have been well documented and it is often criticized for killing beneficial as well as target organisms; hence it is banned in many countries. Still, some agricultural experts argue that equally effective alternatives do not yet exist (Hulshof 1991, PAN 1992, 1994).

1.10. Endosulfan

Endosulfan is a neurotoxic organochlorine insecticide of the cyclodiene family of pesticides. It is highly toxic and an endocrine disruptor, and it is banned in the European Union, Philippine, and several

countries. It is made by Bayer Crop Science, Makhteshim-Agan, and Drexel Company among other, and sold under the trade names Thionex, Thiodan, Phaser, and Benzoepin.

Because of its high toxicity and high potential for bioaccumulation and environmental contamination, a global ban on the use and manufacture of endosulfan is being considered under the stockholm convention (Environmental Health and Alliance, 2007).

1.10.1 Structure:

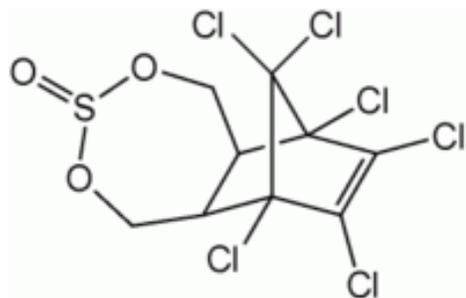


Fig. (1.6): Structure of Endosulfan

IUPAC name: 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9- methano -2,4,3- benzodioxathiepine - 3 -oxide. Molecular formula: C₉H₆Cl₆O₃S.

1.10.2 Properties

Molar mass: 406.95.

Density: 1.745.

Melting point: 70-100 °C.

Solubility in water: 0.33 mg/L.

1.11. Adsorption of endosulfan

Adsorption is one of the most important factors that affects fate of pesticide in soils and determines their distribution in the soil/water environment. Adsorption strongly affects transport processes such as volatilisation to the atmosphere, leaching into groundwater and runoff to surface water (Koskinen and Harper, 1990).

Adsorption occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) (Narayan et. al., 1998). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms.

Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

The amount of adsorption in the soil depends on:

- 1- the type of soil
- 2- the soil conditions (for example temperature, pH, moisture content)
- 3- characteristics of the pesticide.

Soils high in organic matter or clay are the most adsorptive. A pesticide that is adsorbed by the soil is less likely to volatilize, leach or be broken down by microbes. However, it will move with the soil if the soil is eroded. If contaminated soil particles are blown by the wind, or washed away by water, the pesticide may be spread over a great distance (Zupanc et. al., 2002).

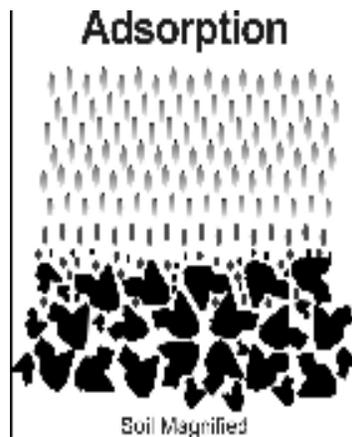


Fig. (1.7): Adsorption process on the soil surface

1.11.1 Adsorption isotherms

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid) (Aly and Faust, 1964).

1.11.1.1 Freundlich Isotherm

Freundlich adsorption equation is used widely in mathematical description of adsorption in aqueous systems. The Freundlich equation is expressed as (Freundlich, 1926).

$$x/m = Kq_e^{1/n}$$

where:

x: amount of solute adsorbed (mg, moles).

q_e : equilibrium concentration of solute.

m: weight of adsorbent, (mg, g).

K: constant, a measure of adsorption capacity.

(1/n): constant, a measure of adsorption intensity.

Estimation of these constants is possible by simple transformation of the eq. above to logarithmic form:

$$\text{Log } x/m = \text{log } K + 1/n \text{ log } q_e$$

Plotting $\log x/m$ versus $\log q_e$, a straight line is obtained with a slope of $1/n$, and $\log K$ is intercept.

1.11.1.2 Langmuir isotherm

In 1916, Irving Langmuir published a new isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
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 (Peterson et. al., 1988).

These four points are seldom true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, the mechanism is clearly not the same for the very first molecules as for the last to adsorb. The fourth condition is the most troublesome, as often more molecules can adsorb on the monolayer, but this problem is solved by the BET isotherm (Kobayashi et. al., 2003).

The Langmuir equation is expressed as (Young and Crowell, 1962):

$$x/m = q_{\max} b q_e / (1 + b q_e)$$

where:

x: amount of solute adsorbed (mg, moles).

m: weight of adsorbent (mg, g).

q_e : equilibrium concentration of the solute.

q_{\max} : amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface (maximum capacity).

b: a constant related to the heat of adsorption. 1/ unit weight.

For linearization of equation, it can be written in the form:

$$q_e / (x/m) = 1/ b q_{\max} + q_e / q_{\max}$$

or

$$1/ (x/m) = 1/ q_{\max} + (1/b q_{\max})(1/ q_e).$$

Any of these equations may be used to evaluate b and q_{\max} from experimental data using graphic or linear least square analysis (Rubin and Mercer, 1981).

1.11.1.3 BET isotherm

Bruner Emmett and Teller (BET) isotherm represents multilayer adsorption.

(BET) equation is commonly written as shown below (Aly and Faust, 1987)

$$x/m = q_{\max} Bq_e / (q_s - q_e) [1 + (B - 1)q_e / q_s].$$

Where: x , m , q_{\max} and q_e have the same meaning as in Langmuir's isotherm. B is a constant describing the energy of interaction between the solute and the adsorbent surface, q_s is the solubility of solute in water at a specified temperature.

1.12 Objectives of this study:

The purpose of this study is to observe the extent of adsorption and desorption of endosulfan on three types soil from different agricultural locations in Palestine.

The effects of the following factors on adsorption and desorption behaviour will be investigated:

1. Soil organic matter content.
2. pH value of the soil samples.
3. Concentration of endosulfan in the liquid phase.
4. Temperature of the soil samples.

A preliminary investigation of the soils properties (texture, organic matter content) have been determined.

CHAPTER TWO
MATERIALS AND METHODS

2. Materials and Methods

2.1 soil

2.1.1 soil sampling

Soil samples of most common soils of Palestine were selected for the study. The soils were identified and classified based on sieve analysis and hydrometer test (ASTM H-152). The organic matter of the soil was determined by chromic acid method (WREP-125 2nd Edition, 1998). The electrical conductivity was measured using conductivity meter (IS 2720 (part 21), 1977). Total soluble solids were estimated from electrical conductivity. The soil pH was measured by using a direct reading type pH meter with glass electrode and calomel reference electrode. The specific gravity was determined by pycnometer method (IS 2720(part3/sec 1), 1987). The moisture percentage of each soil was determined, and taken into account when an exact weight is required for analysis. The properties of the collected soils are given in table (2.1). The soils were sieved through IS (International Standard) sieve No. 10 (2mm aperture as per IS 2720(part 4), 1987). The fraction passing through the sieve was collected and preserved in air tight plastic containers for further studies.

2.1.2 Soil characteristics

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

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

A 0.5 g sample of dried soil was placed in 125 mL Erlenmeyer flask, 5.0 mL of 1.0 N $K_2Cr_2O_7$, 10.0 mL of concentrated H_2SO_4 were added gradually during 1 minute. After 30 minutes 100 mL of distilled water and 0.30 mL of 0.025M ortho-phenanthroline-ferrous complex. A greenish cast colour to dark blue green obtained. The contents titrated against 0.50 N ferrous sulfate solution, until a blue to orange red colour obtained. A blank of $K_2Cr_2O_7$ solution was treated as samples. (WREP-125 2nd Edition, 1998).

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

Organic carbon (%) = $((5 - m_{eq} FeSO_4) \times 0.399) - \text{blank}$ / sample dry weight (g).

T.O.M % = 1.27 x organic carbon %.

2.1.2.2 Texture (Hydrometer Methode)

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: $t = 0.25$ min, 0.5 min, 1 min, 2 min, 4 min, 8 min, 15 min, 30 min, 1 hr, 2 hr, 4 hr, 8 hr, 24 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_c) which is the corrected hydrometer reading for calculation of percent finer = $R + F_T - F_z$.

Column four was the percent finer = $aR_{cp} (100) / W_s$, 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) value from previous tables.

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

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

Soil properties	Red soil	Chalk soil	Sandy soil
Specific gravity	1.469	2.168	2.688
pH value	8.46	7.101	8.5
Electrical conductivity, (E_c), μ_S	230	184.1	84.5
Clay (%)	39	46	2
Silt (%)	61	54	3
Organic matter (%)	9.6	8.4	0.32
Moister content (%)	8	2	0.2

2.2 Chemicals

All chemicals used were analytical grade. Endosulfan was purchased from Sigma Aldrich Ltd.

2.3 Endosulfan standard solutions

A stock 100 ppm solution of endosulfan was prepared by transferring exactly 0.2875 mL of (0.350 g/mL) solution of endosulfan (Thionex®) into a one liter volumetric flask. The volume was completed to the mark with methanol:water solution (70 : 30 % v/v).

2.4 Reaction vessels

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

2.5 Instrumentation

The instrument used for analysis is the UV- Visible spectrophotometer (Shimadzu 1601PC), pH meter (3520 pH meter, JENWAY),

conductometer (4510 conductivity meter, JENWAY), orbital shaker (Remi Instruments Ltd. US).

2.6 The pretreatment of the soil samples

The endosulfan content of the samples used in this work was high compared to the endosulfan concentrations used. Therefore, treating soil samples for desorption of their endosulfan content was necessary before they used. This was done by treating the samples with 0.1 M Perchloric acid (HClO_4) (this acid was chosen because of its ability to remove organic compounds and other metals from soil samples) many times until no traces was found in the extract. Soils were then washed thoroughly with distilled water and stored under distilled water. Portions of these treated samples were taken for the adsorption and desorption experiments.

2.7 Adsorption study

2.7.1 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 1) with a solid: solution mass ratio of 1:20) and 100 ml of 10 ppm of technical endosulfan solution. Sorbent masses were accurate to ± 0.001 g and solution volumes to ± 0.5 ml. The studies were conducted in triplicate for all soils on an orbital shaker (Remi Instruments Ltd.) at 150 rpm for a period of 24 h at room temperature ($25 \pm 2^\circ\text{C}$). From the triplicate flasks, 5

ml of sample was collected at time intervals of 0.25, 0.5, 1, 1.5, 2, 3, 4, 6, 8 and 24 h. The collected samples were filtrated and analyzed by UV-Visible spectrophotometer.

2.7.2. Equilibrium study

Adsorption equilibrium studies were conducted for all soils with an adsorbent quantity of 5 g with technical endosulfan concentrations of 0.1, 0.2, 0.6, 0.8, 1, 2, 4, 6, 8 and 10 ppm in identical conical fasks containing 100 ml of distilled water. A blank was maintained to determine the effect of endosulfan adsorption on the conical fasks. After the addition of soil samples, the reaction mixtures were agitated in an orbital shaker at 150 rpm for 3 h (estimated equilibrium time) at $25 \pm 2^{\circ}\text{C}$. After 3 h, 5 mL of sample was collected from each conical flask, the collected samples were filtrated and analyzed using UV- visible Spectrophotometer.

2.7.3. Desorption

Adsorption equilibrium study was conducted as mentioned earlier. After completion of the adsorption study, the entire reaction mixture was centrifuged and the supernatant in the conical flask was decanted carefully and analyzed for the residual endosulfan concentration.

The same amount of decanted supernatant was replaced with different eluents. Tap water, distilled water and ethanol were the eluents used in this study. The flasks were then kept in an orbital shaker at 150 rpm for a period of 3 h at $25 \pm 2^{\circ}\text{C}$. Soils take long time i.e. days or even

months to attain the adsorption or desorption equilibria, pseudo adsorption equilibrium was attained within 3 h. Hence, the same time was maintained for desorption studies also. After 3 h, 5 mL of sample was withdrawn from the controlled flasks and analyzed for endosulfan concentration using UV-visible spectrophotometer .

2.7.4. Effect of pH on adsorption and desorption of endosulfan in soil samples

A known amount of red, chalk, and sandy soil was used for this study. The initial pH of the soil was adjusted to 1.5, 2, 3, 5, 6 and 7 with concentrated hydrochloric acid (HCl). Five grams of acid treated soil was taken from each pH value and the kinetic study was conducted as stated earlier. Also one of the acid treated soil (pH = 2) was brought up to neutral pH and the kinetic study was conducted. Adsorption kinetic study was conducted with an initial endosulfan concentration of 10 ppm as earlier. The supernatant was decanted and replaced with distilled water of pH 2, 4, 6, 7, 8 and 10 using HCl / NaOH solution and desorption kinetic study was conducted.

2.7.5. Effect of temprature on adsorption and desorption of endosulfan in soil samples

Adsorption equilibrium studies for estimating the effect of temperature on adsorption of endosulfan on soil samples were conducted for all soils with an adsorbent quantity of 5g with endosulfan concentration

of 10 ppm (100 mL) in identical conical flasks, with different temperatures (25, 30, 35, 40, and 45°C). After the addition of the endosulfan solution to the soil samples, the reaction mixtures were agitated in a Heto shaker (SBDO50-1 BIO) for 3 hours at 100 rpm. After 3h, 5mL of samples was collected from each flask, and analyzed using UV-Visible spectrophotometer. The supernatant then treated with ethanol, tap water, and distilled water and desorption kinetic study was conducted on the temperatures 25, 30, 35, 40, and 45°C.

CHAPTER THREE
RESULTS AND DISCUSSION

3. Results and Discussion

3.1 Calibration graph

Standard solutions of endosulfan 0.01, 0.6, 1, 2, 4, 6, 8, 10 ppm were prepared by transferring 0.05, 0.3, 0.5, 1, 2, 3 and 4 mL respectively, from 10 ppm standard solution of endosulfan into 5 ml volumetric flasks and completing the volumes to the mark with methanol :water solution (73:30 % v/v). The absorbances were measured at 214 nm (from previous studies like Wink o. 1985 and Balkom, 1995) against blank solution. A linear relationship was obtained between the absorbance and the concentration of endosulfan within the range (0.1-10 ppm). From the calibration curve (fig. 3.2) the detection limit was found to be 0.01 ppm with an absorbtivity of $(0.129 \text{ l. cm}^{-1}.\text{mg}^{-1})$. And relative standard deviation of (0.524 %) for 5 measurements of (4) ppm.

The calibration curve for endosulfan is shown in figure 3.1.

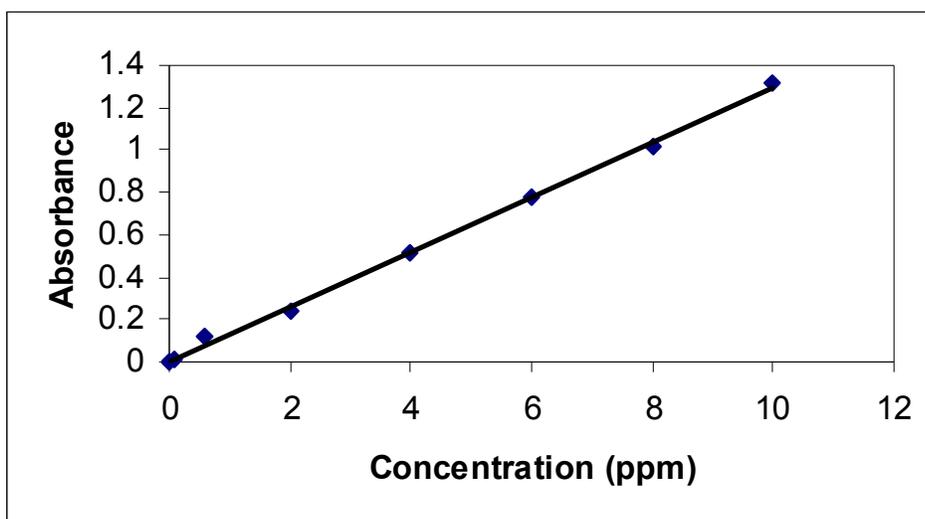


Fig. (3.1): Calibration curve for the estimation of Endosulfan

3.2. Adsorption

3.2.1. Adsorbent—soil samples

The collected soil samples showed a wide variation in clay content Cambodian Agronomic Soil Classification System (CASC) starting from 2% to 46 %. Organic matter (OM) content varied from 0.32 % to 9.6% whereas insignificant variation of pH and specific gravity was observed, (Table 2.1).

3.2.2. Kinetic study

The adsorption kinetics exhibited an immediate rapid adsorption and reached pseudo_ adsorption equilibrium within a short period of 1.5 h in sandy soil and 2 h in chalk soil and 3 h in red soil. After pseudo_ equilibrium, less than 2% variation of endosulfan concentration in the adsorbate was observed even after 24 h. (Fig. 3. 2) 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 h sorption experiments. The rapid initial adsorption of endosulfan is a surface phenomenon. Due to hydrophobic nature of endosulfan, 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). The same trend was observed by Parkpian et.al. (1998) while

studying the adsorption of endosulfan on Rangsit lowland soils and Phrabat upland soils, also by Kumar M., et al. (2006) while studying the adsorption and desorption characteristics of endosulfan in Indian soils.

From the results it is clear that, the sorption of endosulfan 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.

The kinetic rates were estimated by Lagergren pseudo first order model (1898), and Ho's pseudo second order model (1995), given in Eqs. below respectively.

$$\text{Log } (q_e - q_t) = \log q_e - k \cdot t$$

$$(1/q_t) = (1/h) + (1/q_e) \cdot t$$

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; t is the time and $h = k \cdot q_e^2$.

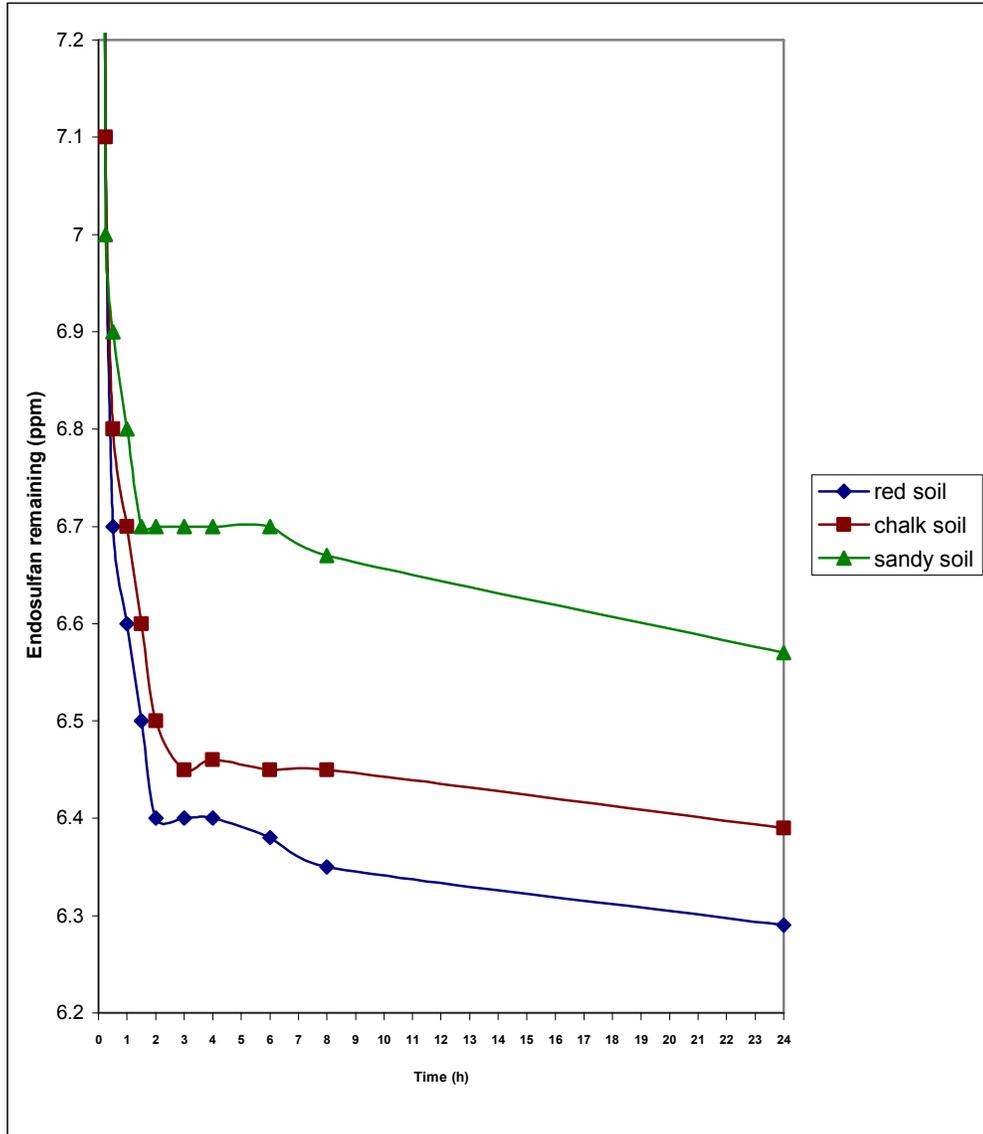


Fig. (3.2): Kinetics of endosulfan adsorption on different soil samples

But none of the above models gave good fit for any of the specimens. This may be attributed to the nonhomogeneity of the soil. Hence, the data were plotted between square root of time ($t^{1/2}$) and equilibrium concentration (q_e).

A tangent starting from the origin was drawn as shown in (Fig. 3.3) and the rate of kinetic equilibrium was calculated as the slope of the tangent.

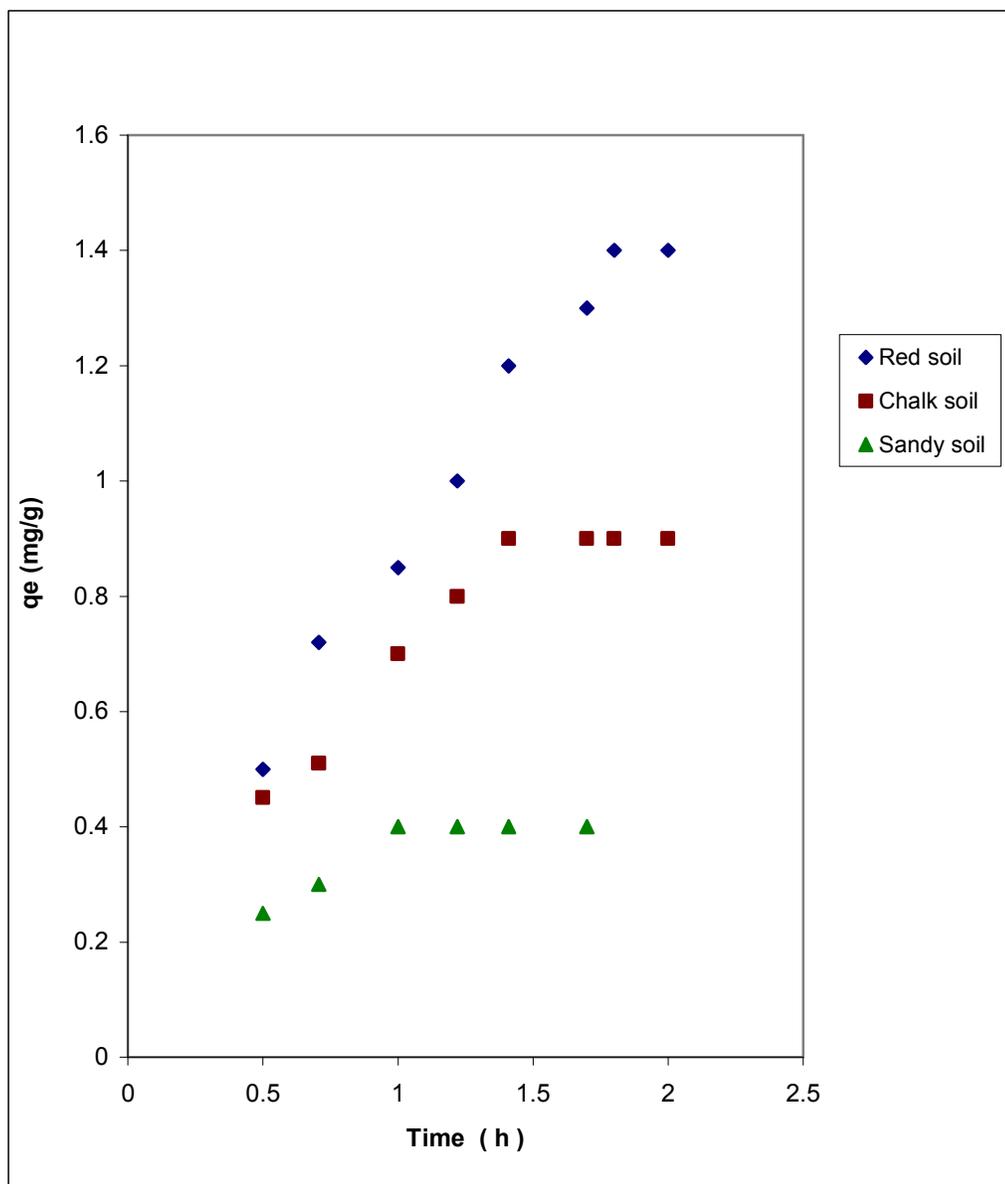


Fig. (3.3): Rate of adsorption of endosulfan on soil samples.

The calculated rate constants for endosulfan $1.56 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for red soil, $1.07 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for chalk soil and $0.0390 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for sandy soil. The kinetic rate constants for different soils are given in (Table 3.1).

Table (3.1): Rate of adsorption of endosulfan

Type of soil	Rate of adsorption (mg g ⁻¹ h ^{-1/2})
Red soil	1.56
Chalk soil	1.07
Sandy soil	0.039

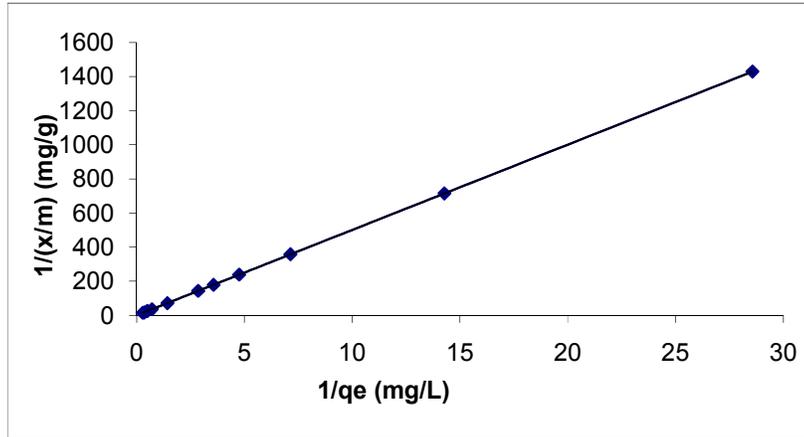
3.2.3. Equilibrium study

In order to find the short term behavior of endosulfan in different types of soils, adsorption isotherm studies were conducted at $25 \pm 2^\circ\text{C}$ with an equilibrium time of 3 h. Using Langmuir

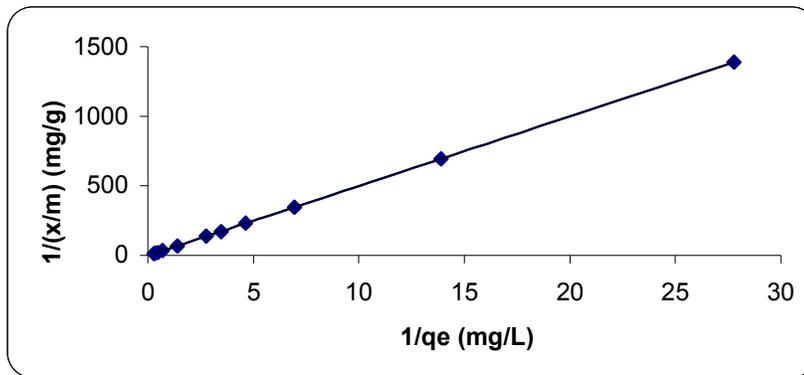
$[(x/m) = (q_{\text{max}} b q_e / (1+bq_e))]$ and Freundlich $[(x/m) = K q_e^{1/n}]$ equilibrium models, where (x/m) (mg/g) is the amount of pesticide adsorbed per gram of adsorbent; q_e (mg/l) is the equilibrium concentration in solution; q_{max} is the maximum adsorption capacity of the adsorbent; b is Langmuir's constant; K 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 (0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 ppm) endosulfan concentrations to understand the behavior clearly. The relation between $1/q_e$ vs. $1/(x/m)$ is shown in (Fig. 3.4), the adsorption of endosulfan followed Langmuir isotherm better than Freundlich 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

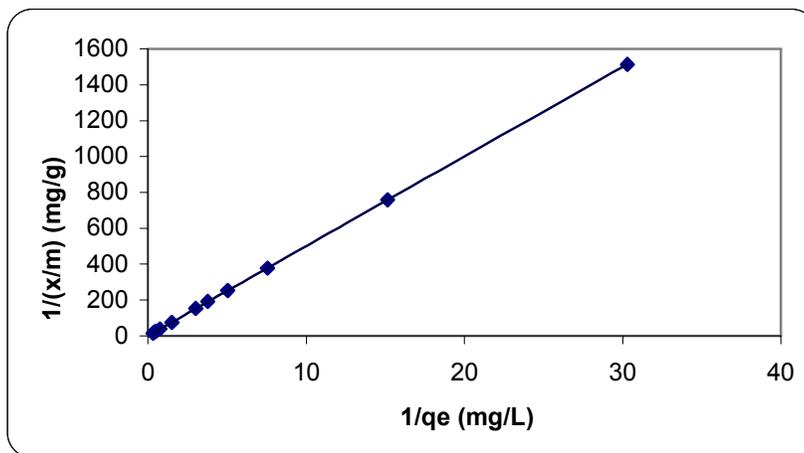
concentration of adsorbate in the solution, which was not sufficient to have a competition for the abundantly available adsorption sites in soil.



(a)



(b)



(c)

Fig. (3.4): Linearized Langmuir isotherm of endosulfan on (a) red soil, (b) chalk soil and (c) sandy soil.

The maximum adsorption (q_{\max}) of endosulfan concentrations occurred in red soil followed by chalk soil, and sandy soil (Table 3.2).

Table (3.2). Adsorption isotherm values for endosulfan by Langmuir and Freundlich isotherms.

Type of soil	Langmuir isotherms		
	q_{\max} (mg/ g)	b	r^2
Red	0.387	1.429	0.965
Chalk	0.218	1.099	0.963
Sand	0.075	0.089	0.9991

Same trend was reported by Torrents and Jayasundera (1997), who conducted the sorption study of non-ionic pesticides and found that the intensity of sorption was a function of herbicide and clay content. The q_{\max} value of red soil for endosulfan was (0.387) mg / g of soil. Red soil has more vacant sites/surface area compared to sand particles (Gao et al., 1998). The organic matter in red soil was (9.6 %), which increased the endosulfan adsorption. On the other hand, sandy soil has fewer pores and adsorption sites (organic matter is 0.2%) which resulted in minimum endosulfan adsorption (0.075 mg /g of soil).

3.3 Effect of organic matter content (OM) on endosulfan adsorption

The properties of chalk soil and red soil were nearly similar but there is difference in OM content (Table 2.1). Though the CASC in the red soil was only 61%; the adsorption of endosulfan was more (0.387 mg /g).

It was noticed that, the OM content in the red soil was 9.6%, which probably influenced the migration of endosulfan molecules to it, (Berglof et al., 2002; Yu and Zhou, 2005). Increase in organic contents increased

sorption of nitroaromatic herbicide dinoseb by either non-specific partitioning or specific charge related mechanisms (Martins and Mermoud, 1998). In addition, the results are in accordance with Iraqi and Iraqi (2000), who demonstrated that beyond 2% organic matter in soils, the adsorption of parathion takes place almost entirely on the organic surfaces. The decrease in OM content which is 8.4 % in chalk soil (as compared to red soil) reduced the adsorption rate of endosulfan from 0.387 to 0.213 mg g⁻¹ h^{-1/2} (Table 3.2). It is important to note that, the extent mineral's contribute to sorption depends on both the ratio of clay minerals and soil organic carbon contents (Hsieh and Kao, 1998; Spark and Swift, 2002). Soil rich in OM may retain the pesticides and reduce the possibility of contaminating the surface and groundwater sources.

3.4 Effect of pH of the soil samples on adsorption

An attempt was made to investigate the significant role played by structure lattice in the adsorption process. The soil samples were digested with acid solution of varying concentrations to disrupt the structure. The pH of the soil samples were brought down to 1.5, 2, 3, 5, 6 and 7 with the use of concentrated HCl. Adsorption kinetic studies were carried out using the treated soil samples with an endosulfan concentration of 10ppm for a pseudo equilibration time of 3 h. The total amount of endosulfan adsorbed on each pH value was shown in (Fig. 3.5). No adsorption of endosulfan was observed at pH 1.5. Above which (between 2 and 3) it increased very slowly. Above pH 3 the trend in adsorption was differ according to soil type as shown in figure below.

Acid treatment destroyed the crystal lattice of the soil particles which might have reduced the adsorption (Kumar M., et al., 2006). To verify the above assumption, acid treated soil with a pH of 2 was neutralized (pH 7.0) and the kinetic study was conducted. The adsorption of endosulfan in the treated soil was only about 0.12 in red soil, (0.09 ppm) in chalk soil, and (0.03 ppm) in sandy soil. From the results the chance of suspicion about regaining of crystal lattice of the soil particles by pH adjustments was eliminated. The adsorption of endosulfan on glassware was insignificant compared to the adsorption of endosulfan in soil.

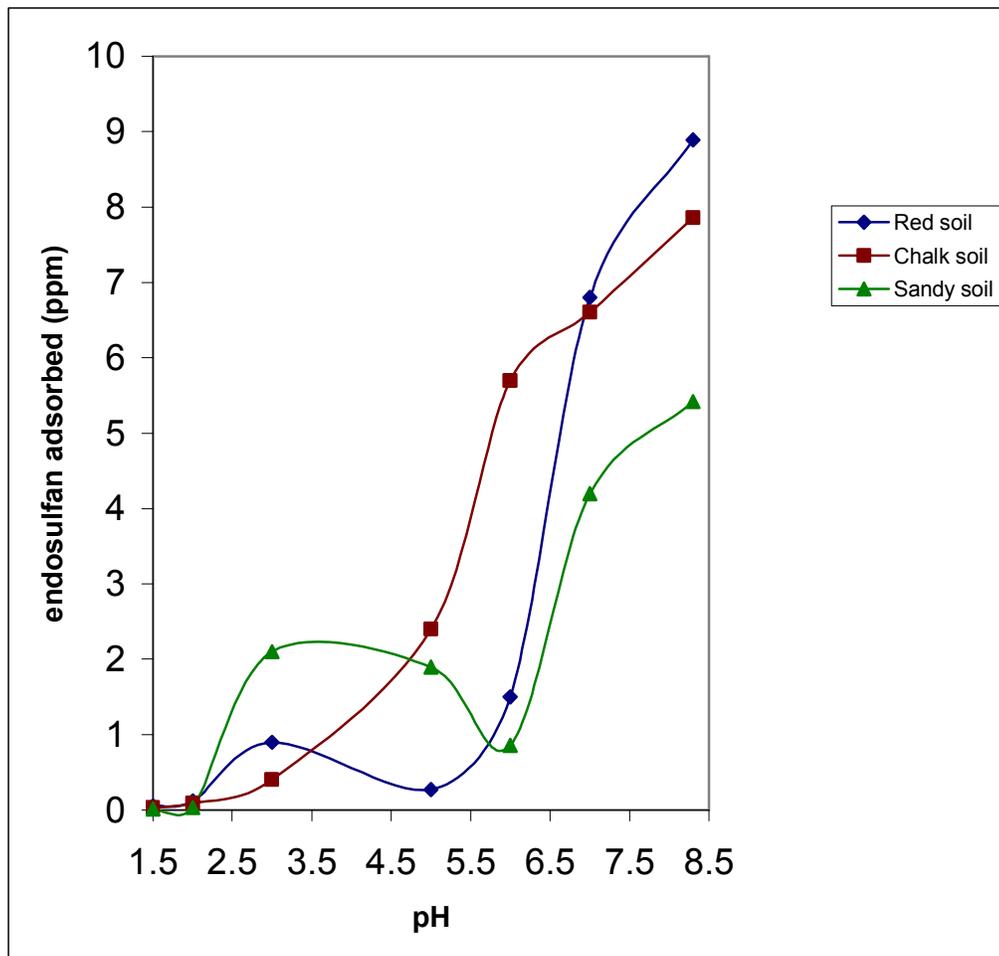


Fig. (3.5): Effect of pH on adsorption of endosulfan on soil samples.

3.5 Effect of concentration of endosulfan on adsorption

From the equilibrium study which was carried out for different concentrations of endosulfan, it was clear that as concentration of the endosulfan solution increased, the amount adsorbed increased as shown in (fig. 3.6).

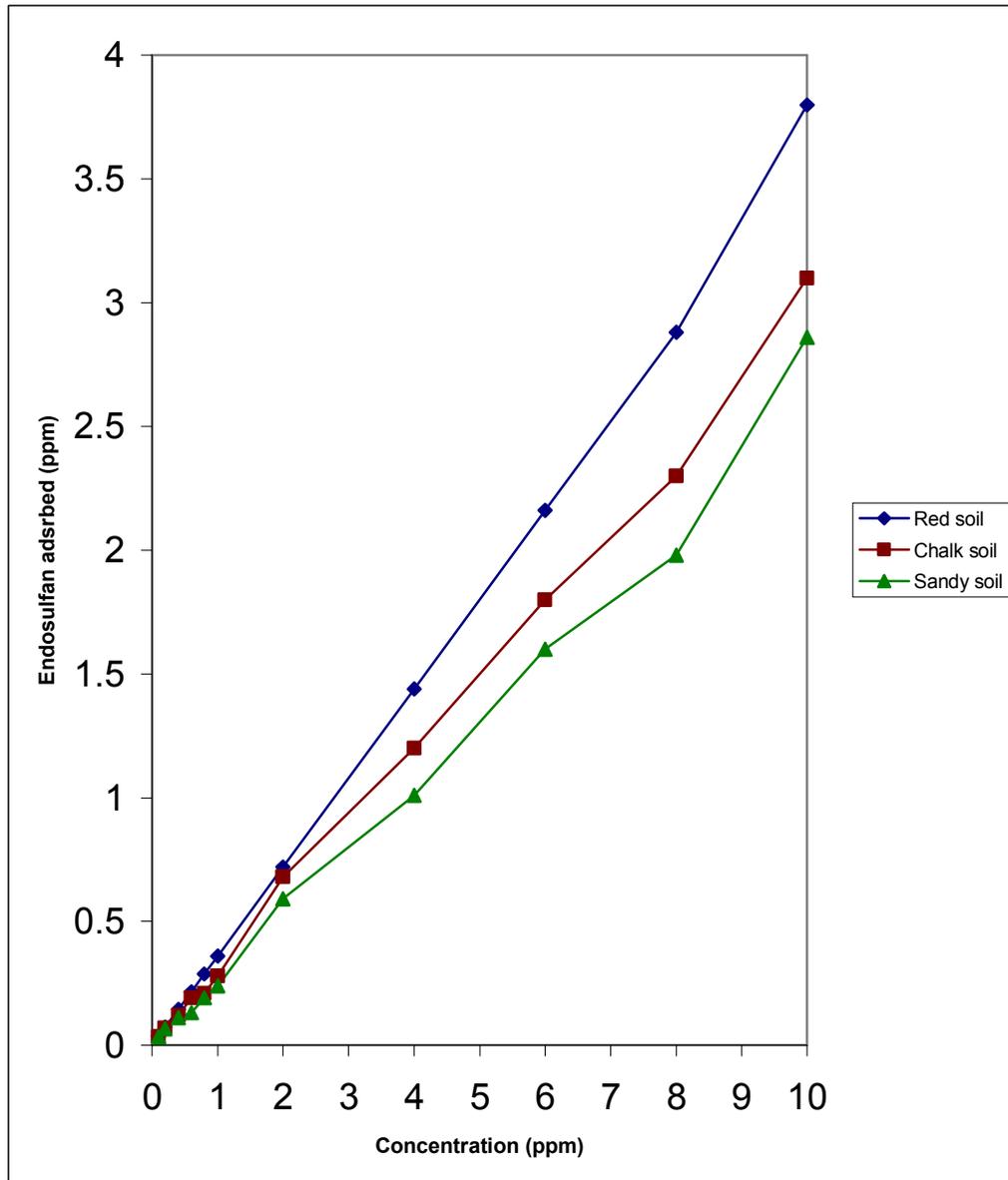


Fig. (3.6): Effect of concentration of endosulfan solution on adsorption of endosulfan on soil samples, (temperature = 25 ± 2 °C).

3.6 Effect of temperature on adsorption of endosulfan on soil samples

Adsorption equilibrium study was conducted to determine the effect of temperature on adsorption of endosulfan on different soil samples. From the results it was clear that the adsorbed amount affected with temperature, and the adsorbed amount increased with the increase in temperature. As shown in (fig.3.7).

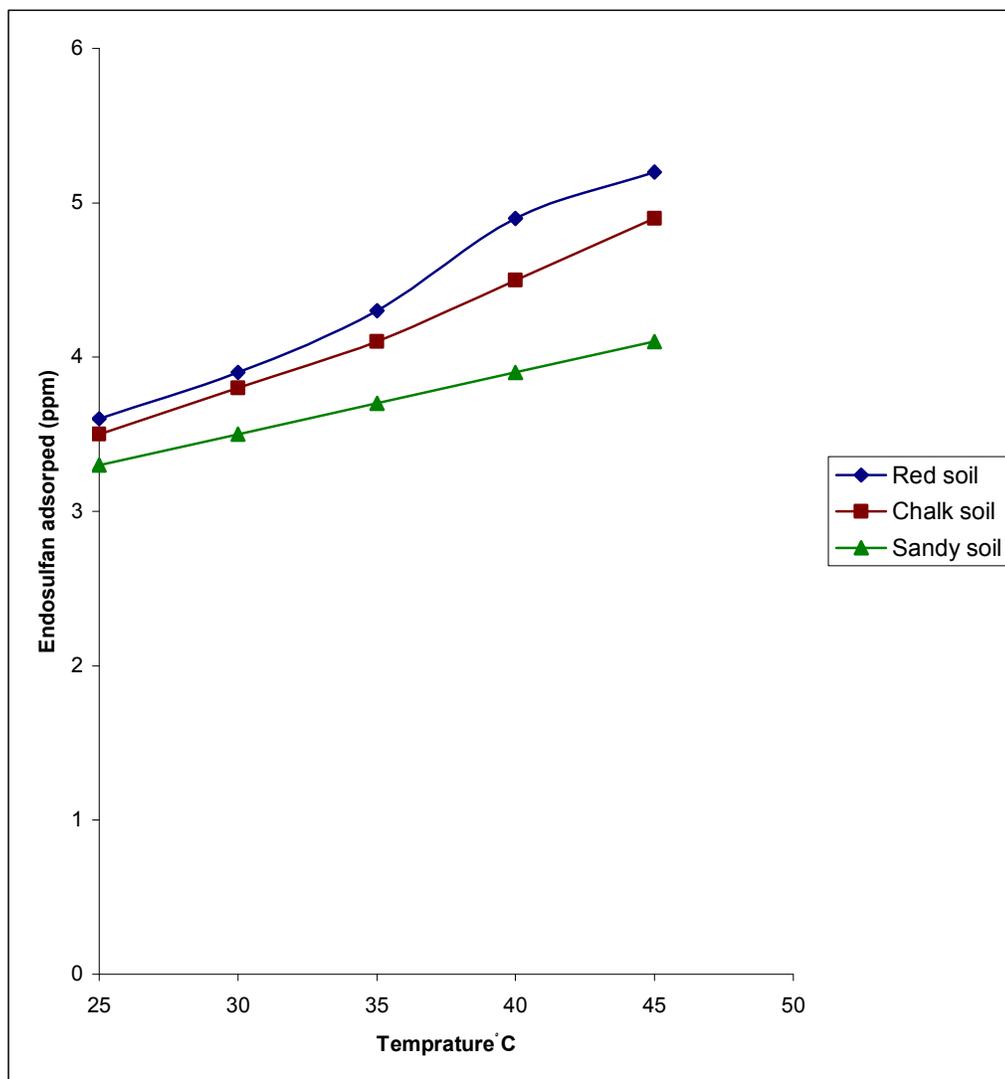


Fig. (3.7): Effect of temperature of endosulfan solution on adsorption of endosulfan on soil samples.

3.7 Desorption

3.7.1. Kinetic study

The mobility of a compound in soil can be assessed from desorption studies. The selection of treatment technique is based on its availability in the liquid phase. Desorption kinetic study was conducted to determine the endosulfan availability in the liquid phase with respect to time. Desorption was rapid in the initial stages and almost attained pseudo equilibrium within 2 h in sandy soil but took relatively longer time (3 h) in red and chalk soils, as shown in figure (3.8). Like adsorption rates, desorption rates were also calculated from the graphs plotted between square root of time ($t^{1/2}$) and desorption equilibrium concentration (q_e) (Fig. 3.9). The calculated values of desorption rates for all soils are given in (Table 3.3) The maximum desorption rate was observed in sandy soil ($0.540 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for endosulfan) followed by chalk soil, and red soil.

Table (3.3): Rate of desorption of endosulfan.

Type of soil	Rate of desorption of ($\text{mg g}^{-1} \text{ h}^{-1/2}$)
Red	0.385
Chalk	0.402
Sand	0.540

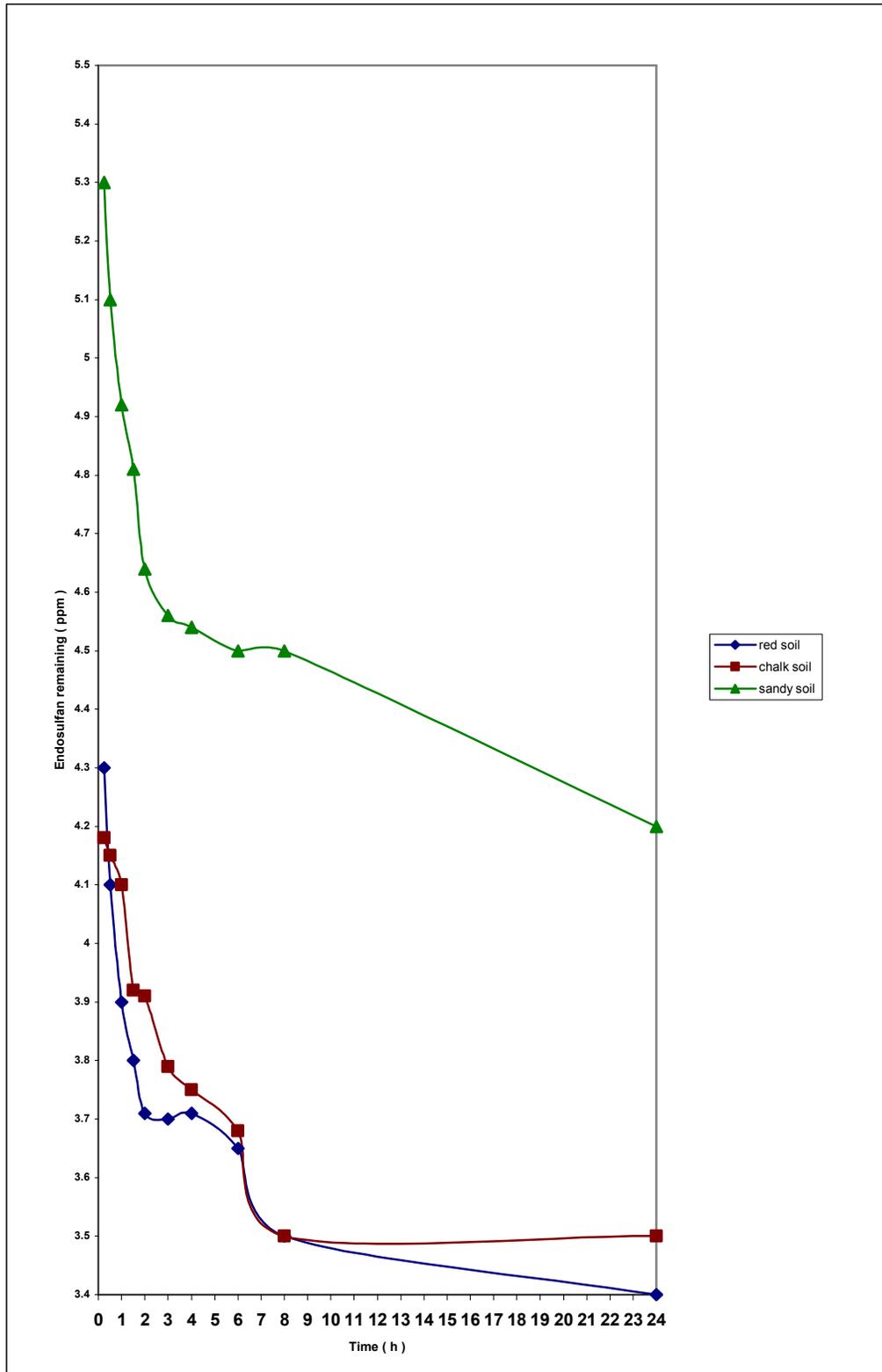


Fig. (3.8): Kinetics of endosulfan desorption on different soil samples

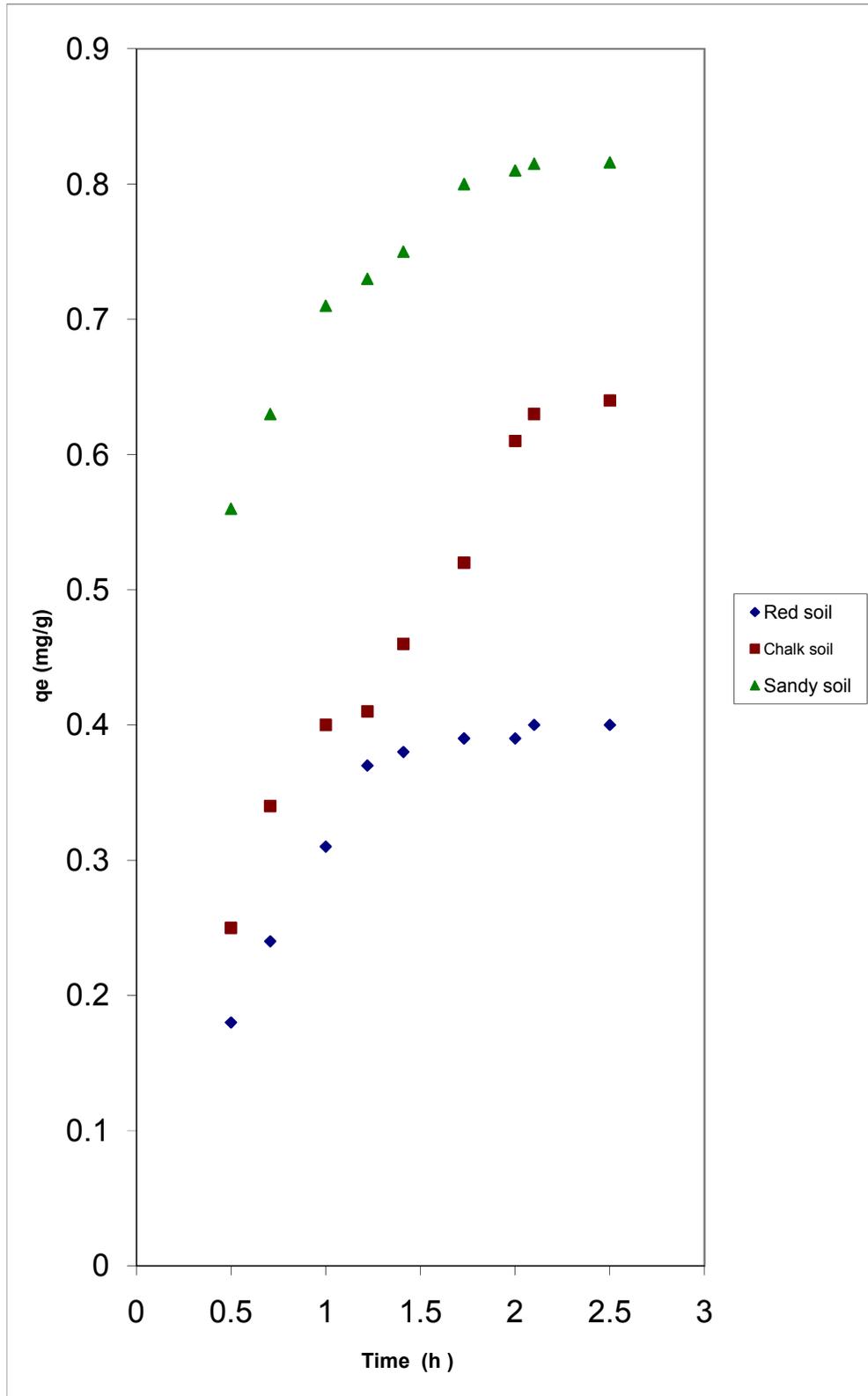


Fig. (3.9): The rate of desorption of endosulfan on soil samples.

3.7.2. Equilibrium study

Equilibrium studies were conducted separately using all soils with a pseudo equilibration time of 3 h (found from kinetic study) and using ethanol, distilled water and tap water. Ethanol showed higher desorption capability for endosulfan in all the soils (Fig. 3.10). On the other hand, distilled water and tap water showed no difference in desorption pattern. Maximum endosulfan desorption of 90% was observed in sandy soil using ethanol as eluent where as ethanol affected only 40% adsorbed endosulfan in red soil.

Distilled water and tap water desorbed only 40% and 38% of adsorbed endosulfan from red soil but desorption was more effective in sandy soil (around 85%) by the use of same eluents. The above findings reflected that adsorption of endosulfan on soil matrix had occurred by the influence of physical and chemical forces however, the influence of them varied from soil to soil.

In sandy soil, adsorption was mainly by physical forces (because of less CASC and OM content) rather than chemical forces (i.e. chemical adsorption is irreversible), which did not shown in red soil, and chalk soil (Berglof et al., 2002). In sandy soil, desorption/mobility of endosulfan was more. Hence, the remediation of endosulfan contaminated sandy soil may be feasible by flushing followed by pump and treat technique.

In red soils, bioavailability and the mobility of endosulfan was less. Immobilization of endosulfan by increasing the clay content can be an

economical and viable treatment option for such type of soils. The increase in organic content of soil decreases the mobility of endosulfan. In situations where the organic matter is soluble and/or easily degradable, can increase the bioavailability of the pesticide. But, organic matters which are relatively xenobiotic, like humic substances, will in turn reduce the bioavailability. Distilled water and tap water are used as eluents to depict the effect of precipitation (rain) on endosulfan migration from contaminated soils. Ethanol is a good solvent for endosulfan. This can affect maximum endosulfan desorption without changing the soil characteristics.

Use of organic solvent ethanol, brought out the rigidly attached endosulfan molecules from the functional groups of the soils and because of that an increase in desorption of 5–10% was observed. Due to strong chemical binding and impartial crystal lattice destruction, a considerable amount of endosulfan was left over in the soil matrix. The complete destruction of the soil crystal lattice can alter the soil properties and lead to some other problems like fertility reduction. The adsorption study results reflected that acids like HCl could completely destroy the structure. So, it was not used as an eluent in the desorption studies. Also, the use of ethanol for a field scale purpose was not a cost-effective process and handling of such an organic solvent in the field will be a limiting factor. On the other hand, tap water was effective in all the soils studied. But considerable amount of endosulfan was left over after the completion of desorption process and this should be given a serious attention.

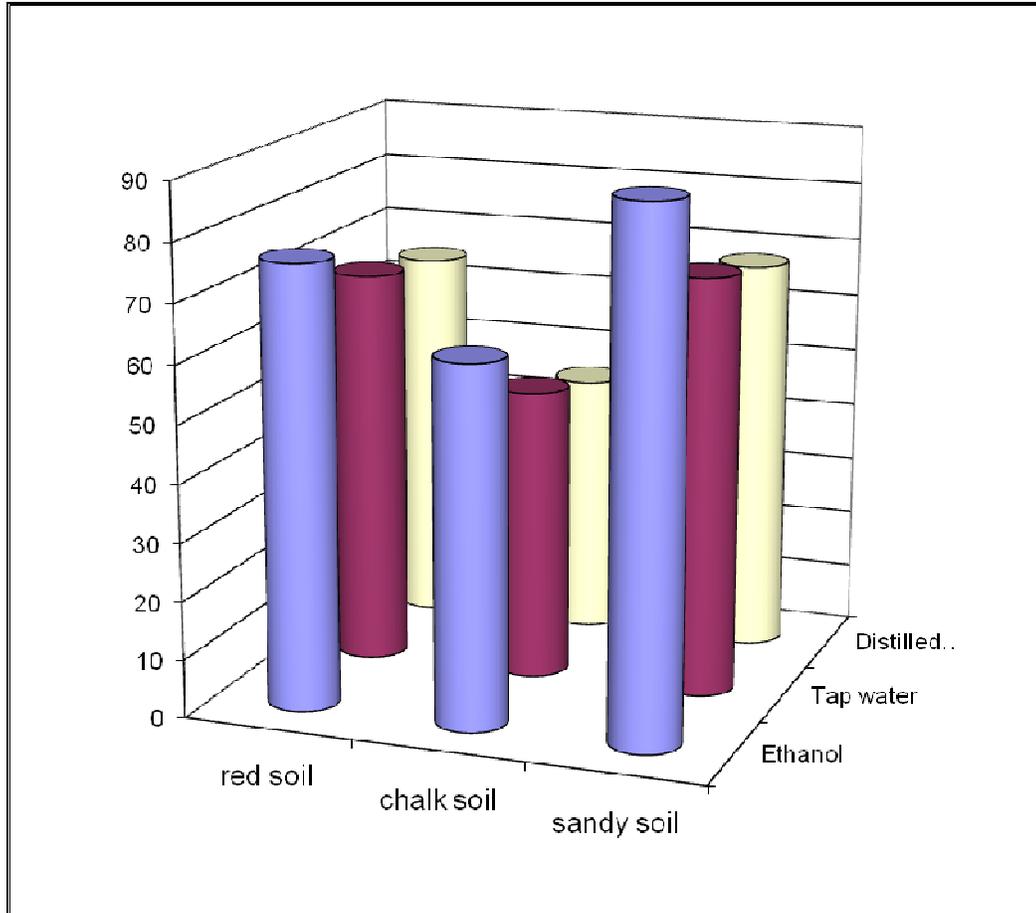


Fig. (3.10): Desorption of endosulfan by different eluents.

3.7.3. Effect of OM on desorption of endosulfan.

Red soil used in this study had more OM % than chalk soil. All other properties of both soils were nearly similar. It was evident from adsorption study that an increase in OM content increased the adsorption rate as well as the adsorption capacity of soil. Like in adsorption, the presence of more OM in red soil compared to chalk soil reduced the endosulfan desorption. It is inferred from the results that, endosulfan molecules were strongly attached to the soil OM which decreased the desorption potential.

3.7.4. Effect of pH on desorption of endosulfan in soil samples.

The effect of pH on endosulfan desorption was investigated using distilled water with various adjusted pH. Desorption kinetic study was conducted for a pseudo equilibrium time of 3 h with an initial endosulfan concentration of 10 ppm. The supernatant was decanted and replaced with distilled water of pH 2, 4, 6, 7, 8 and 10. Desorption kinetic study was conducted for a pseudo equilibrium time of 3 h. At pH 2, desorption was (6.8 ppm) for red soil, (6.1 ppm) for chalk soil, and (8.6 ppm) for sandy soil, and the increase in pH to 4 reduced the endosulfan desorption to (4.82 ppm) for red soil, (5.32 ppm) for chalk soil, (6.71 ppm) for sandy soil. It reduced further to 3.77 ppm in red soil, 4.63 for chalk soil, and 5.42 for sandy soil, and 3.17 for red soil, 3.92 for chalk soil, and 4.13 for sandy soil at pH 6 and 7, respectively. But, endosulfan desorption increased at higher pH values of 8 and 10 (Fig. 3.11). Higher and lower pH might have changed the clay mineralogy or destructed the crystal lattice. This may be the reason for high desorption of adsorbed endosulfan at these pH ranges.

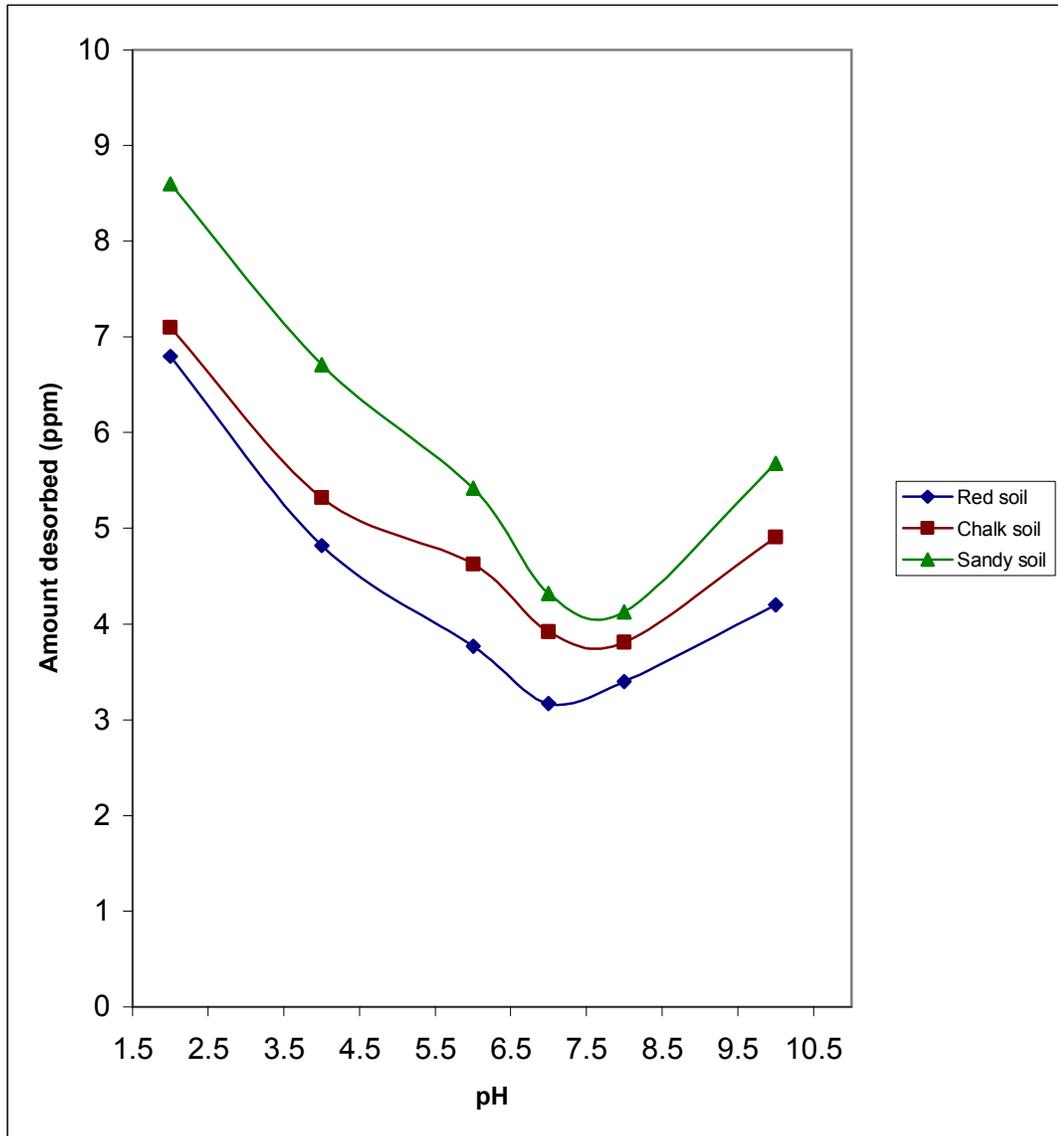


Fig. (3.11): Effect of pH on desorption

3.7.5 Effect of concentration on desorption of endosulfan on soil samples.

Like adsorption experiments, desorption experiments were conducted on soil samples. From the desorption experiments it was found that the amount desorbed increase with the increase in concentration of the endosulfan as shown in (fig.3.12).

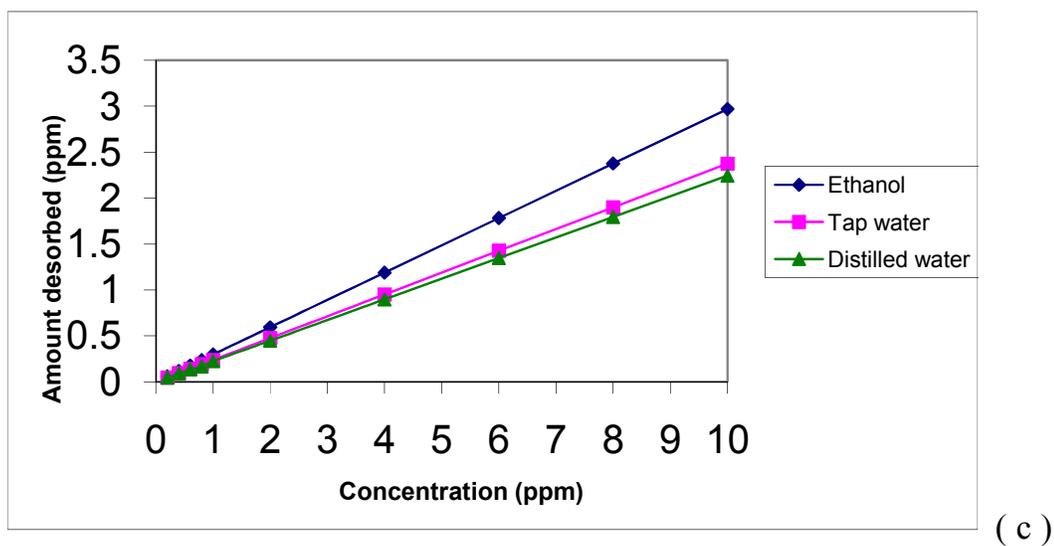
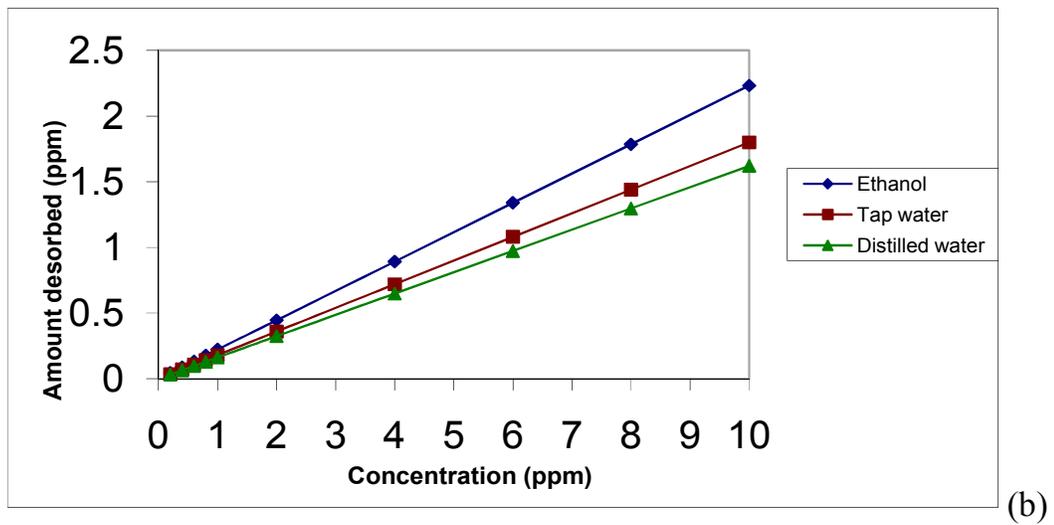
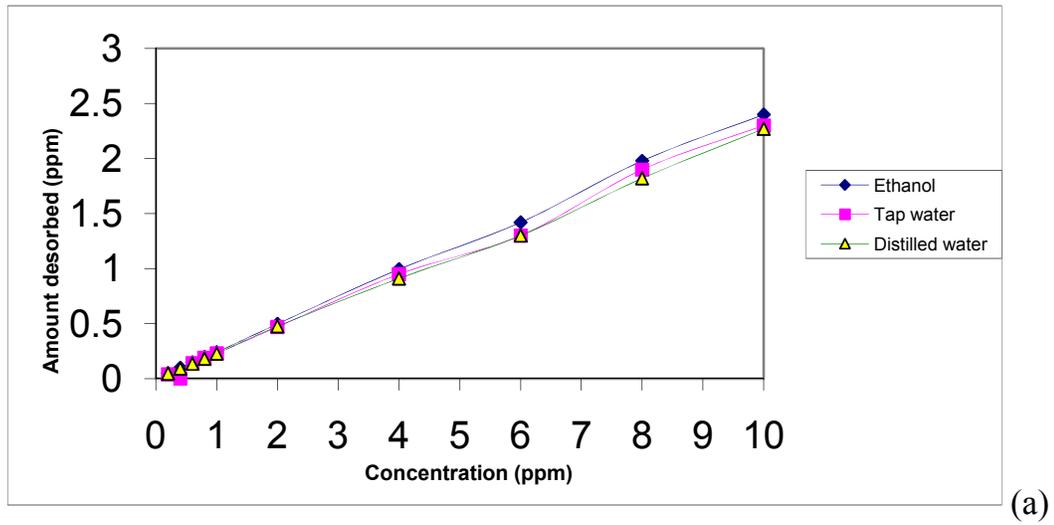
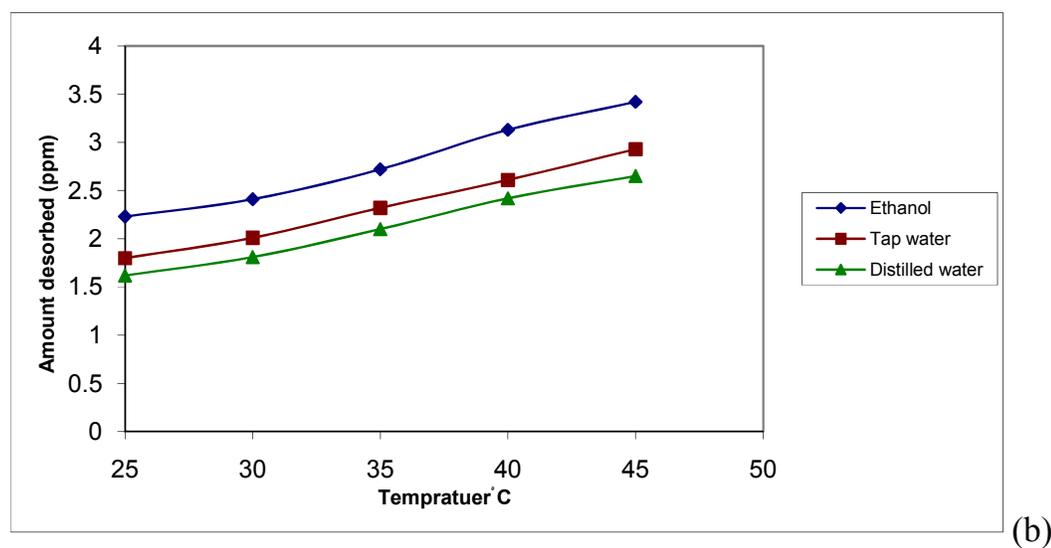
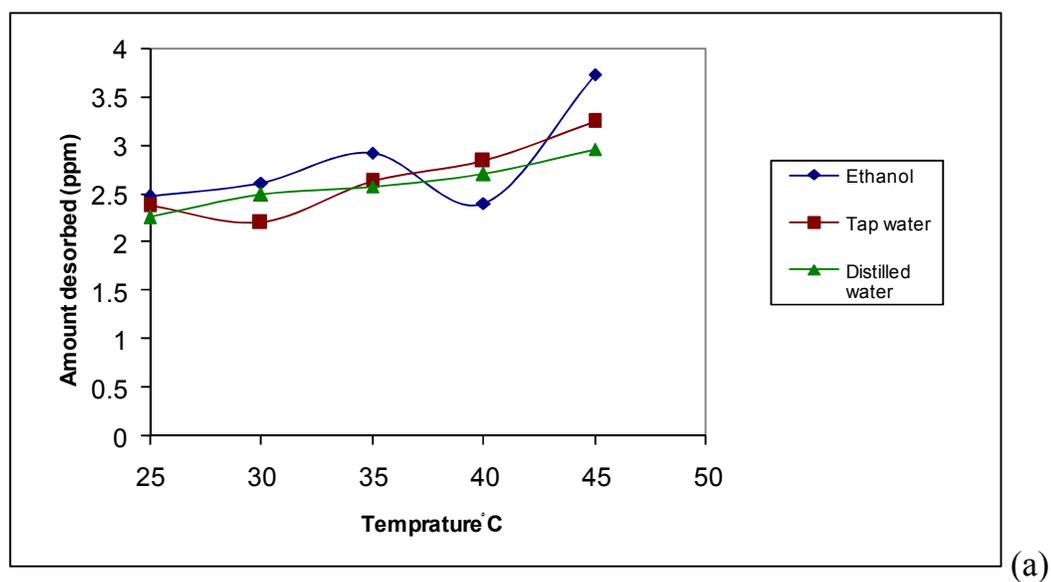


Fig. 3.12 Effect of concentration on desorption of endosulfan on (a) red soil, (b) chalk soil, (c) sandy soil using different eluents.

3.7.6 Effect of temprature on desorption of endosulfan

Desorption equilibrium study was conducted to determine the effect of temperature on desorption of endosulfan on soil samples, with a 10 ppm endosulfan solution in identical conical flasks for different temperatures (25, 30, 35, 40, 45°C). From the results, it was found that the amounts desorped increased with the increase in temperature, as shown in (fig. 3.13).



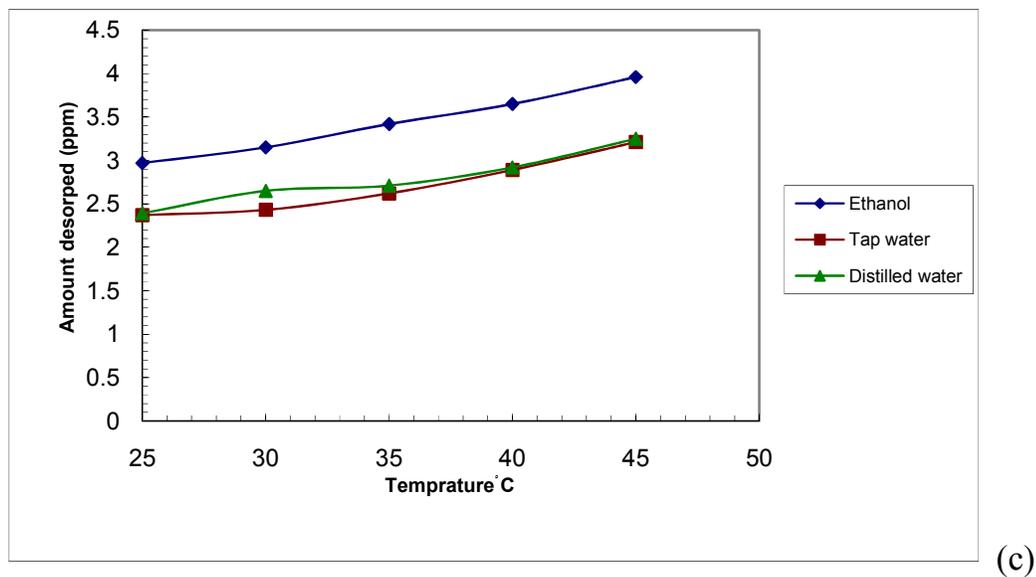


Fig . (3.13): effect of temperature on desorption of endosulfan on (a) red soil, (b) chalk soil, (c) sandy soil, using ethanol, tap water and distilled water as eluents.

CHAPTER FOUR
CONCLUSION AND
RECOMMENDATIONS

4. Conclusion and Recommendations

4.1 Conclusion

The equilibrium rate constant for endosulfan adsorption on soils cannot be calculated by the existing pseudo first order and pseudo second order rate equations because of the non-homogeneity of the soil. Adsorption of endosulfan in all soils followed Langmuir isotherm and it is inferred that the adsorption was monolayer.

Both physical and chemical forces pronounced adsorption. The effect of chemical forces was predominant in red soil and chalk soil. The adsorption of endosulfan towards soil particles was highly influenced by CASC and OM content. Maximum desorption was achieved with ethanol but tap water and distilled water can effectively be used in the field. Narrow variations in the pH of soil medium did not have any influence on endosulfan adsorption or desorption. The decrease in pH of the soil reduced the adsorption.

Both the increase in temperature and concentration increase the adsorption and desorption.

The presence of clay, silt and OM immobilizes endosulfan in the soil. Hence, increasing the CASC and OM content in the contaminated soil/zone can be an alternative solution to prevent the mobility of endosulfan.

4.2 Recommendations

To restrict pesticides getting to soil and affect human through food, the following recommendations can be addressed :

- 1- Pesticides of great danger to human should be identified and used on a very small scale or banned.
- 2- Reduce pesticides when there is no plant covering.
- 3- Soil content of organic matter should be increased by using manure and compost in particular. This will increase the soil biological activity and its ability for adsorption as well.
- 4- Farmers and agricultures should be taught how to care for environment.
- 5- Since endosulfan has two stereo isomers it needs further studies should be conducted to study the kinetics in more details.

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APPENDICES

Appendix 1

Kinetics of endosulfan adsorption on soil samples

Time (h)	Endosulfan remaining (ppm) Red soil solution	Endosulfan remaining (ppm) chalk soil solution	Endosulfan remaining (ppm) sandy soil solution
0	10	10	10
0.25	7.1	7.1	7.0
0.5	6.7	6.8	6.9
1.0	6.6	6.7	6.8
1.5	6.5	6.6	6.7
2	6.4	6.5	6.7
3	6.4	6.45	6.7
4	6.4	6.46	6.7
6	6.38	6.45	6.7
8	6.35	6.45	6.67
24	6.29	6.39	6.57

Appendix 2

Rate of adsorption of endosulfan on soil samples

Time $\frac{1}{2}$ (h) $\frac{1}{2}$	qe (mg/g) for red soil	qe (mg/g) for chalk soil	qe (mg/g) for sandy soil
0.5	0.5	0.54	0.25
0.707	0.72	0.51	0.3
1.0	0.85	0.7	0.4
1.22	1.0	0.8	0.4
1.41	1.2	0.9	0.4
1.7	1.3	0.9	0.4
1.8	1.4	0.9	1.33
2.0	1.4	0.9	1.31

Appendix 3

Langmuir isotherm of endosulfan on soil samples

Red soil		Chalk soil		Sandy soil	
1/ (x/m) 1/(mg/g)	1/qe 1/(mg/l)	1/ (x/m) 1/(mg/g)	1/qe 1/(mg/l)	1/ (x/m) 1/(mg/g)	1/qe 1/(mg/l)
14.285	0.285	13.88	0.277	15.15	0.303
17.357	0.357	17.54	0.347	19.23	0.378
25.00	0.500	23.25	0.462	26.31	0.505
35.714	0.714	35.714	0.694	37.87	0.757
71.428	1.428	69.44	1.388	75.75	1.515
142.85	2.857	138.88	2.770	151.51	3.03
178.57	3.570	173.61	3.472	192.3	3.78
238.09	4.761	231.48	4.629	252.52	5.05
357.14	7.140	347.22	6.944	378.78	7.57
714.285	14.28	694.44	13.88	757.57	15.15
1428.57	28.57	1388.88	27.77	1515.15	30.303

Appendix 4

Effect of pH of the soil samples on adsorption

pH	endosulfan adsorbed (ppm) on red soil	Endosulfan adsorbed (ppm) on chalk soil	endosulfan adsorbed (ppm) on sandy soil
1.5	0.05	0.09	0.01
2	0.12	0.03	0.03
3	0.9	0.4	2.1
5	2.4	2.4	1.9
6	5.7	5.7	0.86
7	6.6	6.6	4.2
8.3	7.86	7.86	5.42

Appendix 5**Effect of concentration of endosulfan on adsorption**

Concentration (ppm)	endosulfan adsorbed (ppm) on red soil	endosulfan adsorbed (ppm) on chalk soil	endosulfan adsorbed (ppm) on sandy soil
0.1	0.036	0.035	0.033
0.2	0.072	0.069	0.066
0.4	0.144	0.12	0.11
0.6	0.216	0.19	0.13
0.8	0.288	0.21	0.19
1.0	0.36	0.28	0.24
2.0	0.72	0.68	0.59
4.0	1.44	1.2	1.01
6.0	2.16	1.8	1.6
8.0	2.88	2.3	1.98
10.0	3.8	3.1	2.86

Appendix 6**Effect of temperature on adsorption**

Temperature (°C)	endosulfan adsorbed (ppm) on red soil	endosulfan adsorbed (ppm) on chalk soil	endosulfan adsorbed (ppm) on sandy soil
25	3.6	3.5	3.3
30	3.9	3.8	3.5
35	4.3	4.1	3.7
40	4.9	4.5	3.9
45	5.2	4.9	4.1

Appendix 7

Kinetics of endosulfan desorption on soil samples

Time (h)	Endosulfan remaining (ppm) Red soil solution	Endosulfan remaining (ppm) chalk soil solution	Endosulfan remaining (ppm) sandy soil solution
0.25	4.3	4.18	5.3
0.5	4.1	4.15	5.1
1.0	3.9	4.10	4.92
1.5	3.8	3.92	4.81
2.0	3.71	3.91	4.64
3.0	3.7	3.79	4.56
4.0	3.71	3.75	4.54
6.0	3.65	3.68	4.50
8.0	3.5	3.5	4.50
24	3.4	3.5	4.20

Appendix 8

Rate of desorption of endosulfan on soil samples

Time $\frac{1}{2}$ (h) $^{\frac{1}{2}}$	qe (mg/g) for red soil	qe (mg/g) for chalk soil	qe (mg/g) for sandy soil
0.5	0.18	0.25	0.56
0.707	0.24	0.34	0.63
1.0	0.31	0.4	0.71
1.22	0.37	0.41	0.73
1.41	0.38	0.46	0.75
1.7	0.39	0.52	0.8
1.8	0.4	0.61	0.81
2.0	0.4	0.63	0.815

Appendix 9

Desorption of endosulfan by different eluents

Amount desorped from red soil (ppm)			Amount desorped from chalk soil (ppm)			Amount desorped from sandy soil (ppm)		
With ethanol	With Tap water	With Distilled water	With ethanol	With Tap water	With Distilled water	With ethanol	With Tap water	With Distilled water
2.4	2.3	2.27	2.232	1.8	1.62	2.97	2.376	2.244
1.98	1.9	1.82	1.785	1.44	1.296	2.376	1.9	1.795
1.42	1.3	1.3	1.339	1.08	0.972	1.782	1.4256	1.346
0.994	0.95	0.91	0.892	0.72	0.648	1.188	0.9504	0.8976
0.497	0.47	0.476	0.446	0.36	0.324	0.594	0.4752	0.448
0.24	0.23	0.227	0.223	0.18	0.162	0.297	0.2376	0.224
0.198	0.19	0.18	0.178	0.144	0.129	0.2376	0.19	0.167
0.149	0.14	0.091	0.133	0.108	0.097	0.178	0.142	0.134
0.099	0.09	0.0455	0.089	0.072	0.064	0.1188	0.095	0.089
0.0497	0.04	0.014	0.044	0.036	0.0324	0.0594	0.047	0.044
0.024	0.023	0.014	0.022	0.018	0.016	0.0297	0.0237	0.0224

Appendix 10

Effect of pH of the soil samples on desorption

pH	endosulfan desorbed (ppm) on red soil	Endosulfan desorbed (ppm) on chalk soil	endosulfan desorbed (ppm) on sandy soil
2	6.8	7.1	8.6
4	4.82	5.32	6.71
6	3.77	4.63	5.42
7	3.17	3.92	4.32
8	3.4	3.81	4.13
10	4.2	4.91	5.68

Appendix 11**Effect of temperature on desorption**

Temperature (°C)	endosulfan desorbed (ppm) on red soil			endosulfan desorbed (ppm) on chalk soil			Endosulfan desorbed (ppm) on sandy soil		
	With ethanol	With Tap water	With Distille d water	With ethanol	With Tap water	With Distille d water	With ethanol	With Tap water	With Distille d water
25	2.23	1.8	1.62	2.48	2.38	2.27	2.97	2.37	2.39
30	2.41	2.01	1.81	2.62	2.21	2.49	3.15	2.43	2.65
35	2.72	2.32	2.1	2.93	2.63	2.58	3.42	2.62	2.71
40	3.13	2.61	2.42	2.41	2.84	2.71	3.65	2.89	2.92
45	3.42	2.93	2.65	3.74	3.25	2.97	3.96	3.21	3.25

جامعة النجاح الوطنية

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إشراف

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قدمت هذه الأطروحة استكمالاً لمتطلبات درجة الماجستير في الكيمياء بكلية الدراسات
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2009م

ب

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المخلص

تم في هذه الأطروحة دراسة خاصية الادمصاص (adsorption) وخاصية نزع الملوّث من التربة (desorption) بشكل مفصل في ثلاث عينات من تربة فلسطين، حيث شملت العينات على تربة حمراء وطباشيرية وتربة رملية حسب مقياس ASTM لتصنيف التربة. كما تم في هذه الدراسة حساب معدل الادمصاص ومعدل نزع الملوّث من عينات التربة، وكان معدل اختلاف القيم بناء على نوع التربة.

تم حساب القيمة العظمى للادمصاص (Maximum specific adsorption capacities (q_{max}) باستخدام نموذج لانجموير (Langmuir)، وكانت على النحو التالي: للتربة الحمراء (0.387)، و(0.281) للتربة الطباشيرية، و (0.075) ملغ اغم للتربة الرملية.

أكثر امتصاص تم قياسه كان في التربة الحمراء يليها الطباشيرية، أما بالنسبة للتربة الرملية فقد سجلت القيمة الأقل في الادمصاص. كذلك فإن نسبة المادة العضوية تلعب دوراً كبيراً في كل من عمليتي الادمصاص ونزع الملوّث من التربة.

حدث انخفاض كبير في عملية الادمصاص في عينات التربة بالمقارنة مع الانخفاض في درجة الحموضة (pH) للتربة، أما بالنسبة لعملية نزع الملوّث فقد أظهرت قيماً مرتفعة سواء في الوسط الحامضي أو القاعدي مقارنة بقيمتها عند قيمة التعادل لدرجة الحموضة، كذلك فإن الزيادة في كل من درجة الحرارة وتركيز الملوّث أدت إلى ارتفاع قيمة الادمصاص وعملية نزع الملوّث من التربة.

ج

أخيراً، أظهرت النتائج أن نسبة حركة الملوّث كانت أكثر ما يمكن في التربة الرملية تليها الطباشيرية تليها الحمراء وقد يُعزى ذلك إلى طبيعة تركيب بلورة التربة الحمراء التي تلعب دوراً مهماً في كلتا العمليتان، كما انه يمكن أن يكون هناك دوراً كبيراً للعمليات البيولوجية والكيميائية التي تلعب دوراً في عينات التربة الأخرى.