UNIVERSITY OF NAIROBI

DEPARTMENT OF CHEMISTRY

ADSORPTION CHARACTERISTICS OF CAPTAFOL PESTICIDE BY SEDIMENT AND SOIL SAMPLES: APPARENT THERMODYNAMIC PROPERTIES USING SPECTROSCOPIC METHODS

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Research thesis submitted in partial fulfilment of the Degree of Master of Science in Analytical Chemistry of the University of Nairobi

2014

DECLARATION

This thesis is my original work and has not been submitted for a degree in any university.

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DEDICATION

To my grandfather Elphas Birgen, mother Kesiah Singoei and my son Asier Kiptoo.

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ABSTRACT

This study involved adsorption of captafol on red soil obtained from Kwale county and the sediments collected from Ngong river, by varying the initial concentration of the adsorbate, shaking time and weight of adsorbent. The sediment collected from Ngong river and the red soil obtained from Kwale county used were analysed for pH, texture, cation exchange capacity and organic carbon content. The adsorption was determined by measuring concentration of the pesticide using UV-Vis-NIR spectrophotometer before and after the attainment of equilibrium..Freundlich and Langmuir adsorption isotherms were used to study adsorption behaviour of the pesticide at equilibrium conditions. The relationship between sediments and soil characteristics and thermodynamic properties was explored following Gibbs free energy expressions.

Captafol was found to absorb at 442 nm. A calibration for captafol showed a linear relationship for concentration range from 0.2 to 40 ppm, and slight deviation as the concentration increased to 100 ppm. This was in accordance with the Beer's law.

Freundlich isotherm fitted well for most of the data. Adsorption rate for captafol for red soil was found to be 0.035 g mg/min and 0.0245 m mg/min for sediment. Thermodynamics parameters showed that adsorption process was exothermic and spontaneous. Gibbs energy (ΔG), apparent equilibrium constant (K') and number of adsorption sites (n) were some thermodynamic properties investigated. The calculated values for K' were 57.34±4.6 and 58.16±4.7, ΔG: -9.98±0.19 (kj/mol) and -10.05±0.21 (kj/mol), n: 1.08±0.03 and 1.10±0.01 for the sediment and red soil, respectively.

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ABBREVIATIONS

2,4-D- 2,4-dichlorophenoxyacetic acid

CASC- cambodian agronomic soil classification system

CEC- cation exchange capacity

DDT- dichlorodiphenyltrichloroethane

IPM- integrated pest management

Kd-adsorption distribution coefficient

MCPA- methylchlorophenoxyacetic acid

OC- organic carbon

OM- organic matter

PCP- pentachlorophenol

PCPB- pest control products board

TCE- trichloroethene

USEPA- united state environental protection agency

UV-Vis-NIR - ultra violet visible near-infra red

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

The production and utilization of pesticides is increasing all over the world on daily basis as food demands increase due to population increase. It is worth noting that when pesticides are applied to the field, it is only a small portion which reaches its target while the remaining large part is released into the environment. This may lead to problems, such as leaching, toxicity to non-target organisms and accumulation. Pollution of the soil, ground and surface waters involve risk to the environment as well as to human health due to the possibility direct or indirect exposures [Bajeer *et al.*, 2012].

Plant protection chemicals such as pesticides contribute one of the most important agricultural inputs. Being a damage- and risk-reducing input, these products are oftenly used as their demand is inelastic. Their stochastic nature (climatic conditions, productivity and pest arrival) is related to uncertainty on the timing and the way of applying them. Additionally, application of pesticide is related to various externalities that demand for an immediate utilization of the chemical substances. Pesticide risk valuation studies in conjunction with Integrated Pest management (IPM) strategies provide the means of alleviating the above mentioned externalities.

The following figure 1.1 below gives a brief summary of the positive use of pesticides today in the world.

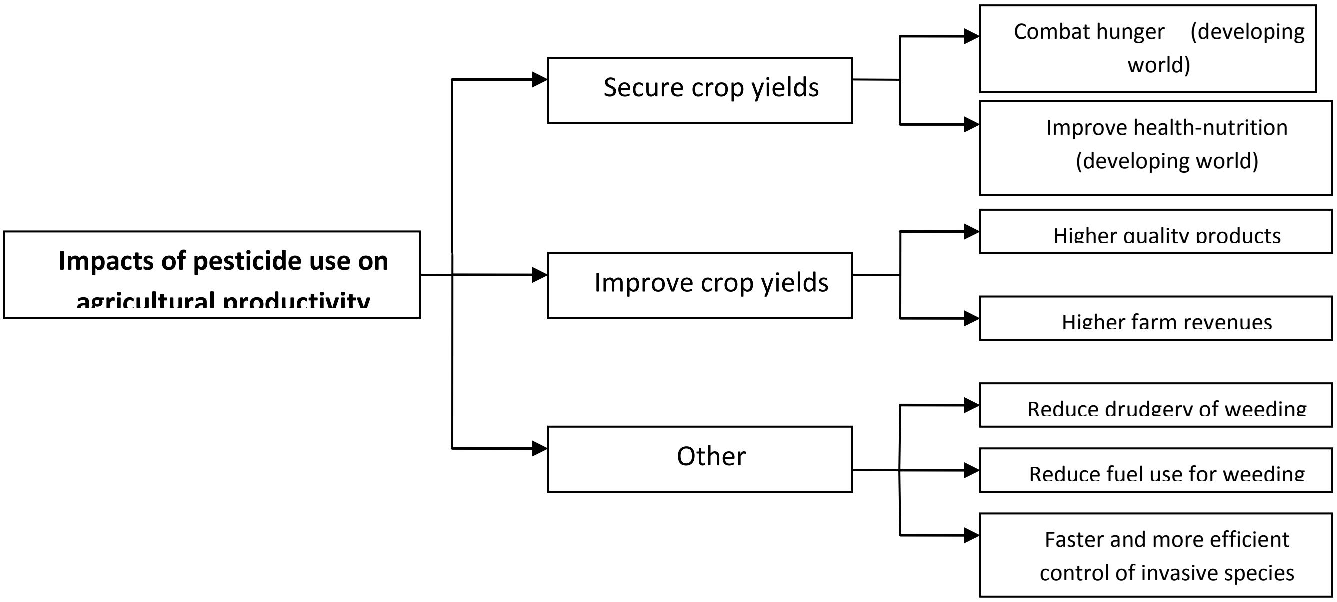

Figure 1.1: Environmental impacts of agricultural intensification [Skevas 2008].

In modern agricultural practices, efficiency and cost minimization is of the utmost importance. For instance, the control of weeds and other unwanted plant growth. Pesticides have been used all over the world for many years now. In Kenya, many farmers are heavily relying on various types of pesticides to boost their production [Taiti, 2010]. With the continued use of pesticides, some accumulate in the soil and related environmental areas. This can lead to serious problems to crops sown later and also to the people who consume these crop products.

The objective of this study was to determine the effect of pesticide concentration, the quantities of the soil sample and the shaking time to the adsorption of diquat dibromide pesticide.

1.2 Pesticide History and Classification

A pesticide is any substance used to kill, repel, or control certain forms of plant or animal that are considered to be pests. A pest on the othe hand is any organism that damages crops, injures or irritates livestock or man, or reduces the fertility of the soil. There are many types of pesticides that are commonly used. These include; herbicides for destroying weeds and other unwanted vegetation, insecticides for controlling a wide variety of insects, fungicides used to prevent the growth of molds and mildew, disinfectants for preventing the spread of bacteria, and compounds used to control mice and rats. 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 use has greatly improved agricultural productivity by minimizing loses due to infestastion by pests. For instance in the US, farmers get an estimated four fold return on money they spend on pesticides [Kollogg *et al.*, 2000]. The use of pesticides is constantly increasing and has become popular among farmers. One study found that the use of pesticides increased by 7% between 1996 and 2011 [Benbrook, 2012].

Pesticides have been used by human for a very long time. Since the beginning of agriculture, various forms were used to control pests. Notably use of salt, smoke and animals were used in ancient times. Sumerians in 2500 B.C used elemental sulfur to protect their crops from insects. The Medieval farmers and scientists experimented to control these pest by use of chemicals ranging from arsenic to lead on common crops. The Greeks and Romans used oil sprays, ash and sulfur ointments and also lime to protect themselves and their crops [Cunningham *et al.*, 2003]. In the nineteenth century research focused more in natural techniques involving compounds made with roots of tropical vegetables and chrysanthemums. Chemical pest control era began in early 1930’s. Dichloro-diphenyl-trichloroethane was discovered by Paul Muller, a Swiss chemist. It was dicovered to be extremely effective and was wiidely used in Switzerland to control potato beetles in 1939. In early 1940s, manufacturers began to produce large amounts of synthetic pesticides and their use became widely spread all over the world. DDT made a revolution in the world, it became an efficient and stable compound that was easily spread over a wide area. It was effectively used in tropical countries to combat the *anopheles* mosquito, which transmits malaria. In 1944, the first hormone based pesticide, 2,4-D, was introduced. Two years later, Switzerland reported the first case of pesticide-resistance, houseflies were not being affected by DDT anymore. During the 1950's and 1960's there were numerous reports on DDT resistant plagues. Rachel Carson [1962], in her book "*Silent Spring*" created an awareness revolution by pointing out pesticides as the reason for the systematic poisoning of the ecosystem that ultimately reduced the bird population due to egg shell defects. In the following years (1973-1975) new types of pesticides were developed such as synthetic pyrethroids. During that time, new approaches such as "integrated pest management" were developed and adopted throughout the world to reduce pesticide consumption and increase efficiency in the control of pests [Carson, 1962].

Pesticide use has increased 50 fold since 1950 and 2.5 million tonnes (2.3 million metric tonnes) of industrial pesticides are now used each year [Miller, 2002]. DDT is now banned in at least 86 countries, although it is still being used in some developing nations to prevent malaria and other tropical diseases by killing disease carrying insects [Lobe, 2006].

1.3 Pesticides Effect On Soil

The use of pesticides can degrade the soil and can also cause damage to microorganisms if misused or overused. Although some pesticides may break down quickly when applied to soils, others may persist for longer periods. Pesticides are important, but their influence on nontarget organisms are of great concern since this poses a high risk to the entire ecological system [Kalia and Gupta, 2004]. The effects of pesticides on soil and soil microorganisms will vary depending on the soil properties, chemical dosage, and various environmental factors [Ecobichon, 1991]. The application and pesticides use has led to a rapid decline in the quality of the organic matter in the soil. A significant portion of chemicals utilized in pesticides are persistent soil contaminants, which may cause negative impact lasting for decades and adversely affect soil conservation [USEPA, 2007].

1.4 Effect of Pesticide on Soil Quality

Soil's capacity to buffer, filter, degrade, detoxify and immobilize pesticides is a quality or a function of the soil [Cameron *et al.*, 1996]. Soil quality impacts on air and water quality and on the human and animal health [Stolze *et al.*, 2000]. Bioavailability and presence of pesticides in the soil can also impact on human and animal health, and beneficial plants and soil organisms. In addition, pesticides drift contaminate ground and surface water sources and possibly cause adverse impacts on the aquatic ecosystems [Jaenicke, 1998].

1.5 The Fate of Pesticides in the Environment

Once pesticides are applied to offices, homes, lawns, fields, gardens and water sources they become mobile in the environment. Several factors determine how a pesticide will move once in the environment. A pesticide stays in the applied area for a long time sufficient to produce the desired effect and then degrades into harmless materials [Miller, 1993]. Three modes of degradation occur in soils: 1) biological breakdown by microorganisms; 2) Chemical breakdown by chemical reactions, such as hydrolysis and redox reactions; and

3) Photochemical breakdown by ultraviolet or visible light.

The time it take a chemical to break down is expressed as the half life, which is the the time required for half of the atoms of a given amount of radioactive substance to disintegrate. The half life of a pesticide depends on its formulation, soil type and the environmental conditions, such as temperature and moisture. If a pesticide moves off-site (through leaching, wind drift or runoff), it is considered to be pollutant [Conrado *et al.*, 2002]. The potential for pesticides to move off site depends on the formulation and chemical properties of the pesticide, rate and mode of application, soil properties, pesticide persistence, timing and frequency of rainfall or irrigation as well as the depth to ground water (Sparks, 2003). These processes are summarized in Figure 1.2 below.

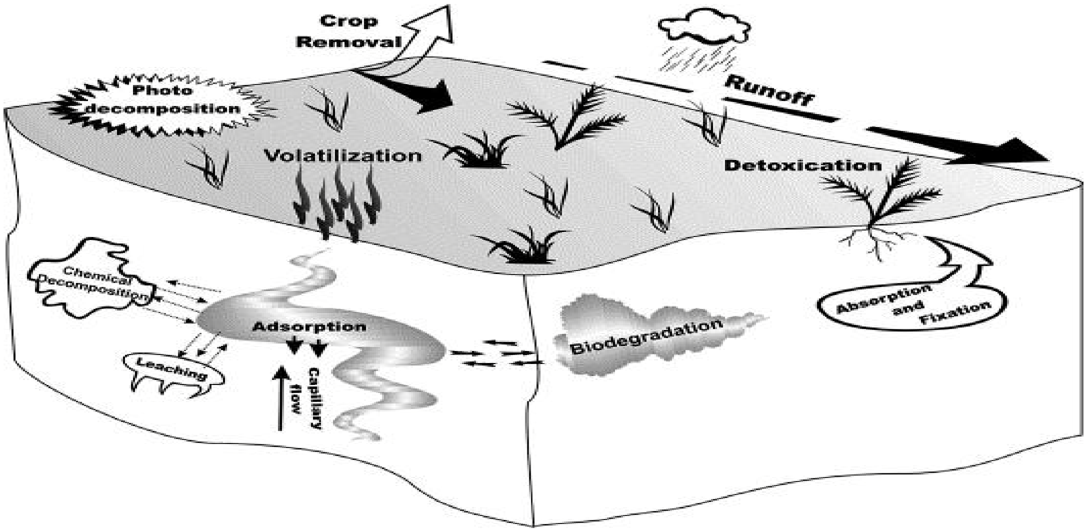

Figure 1.2: Fate of pesticides in soil.

1.6 Retention of Pesticides In The Soil

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

1.7 Pesticides Usage in Kenya

Agriculture is the backbone of the Kenyan economy. It contributes 24% of the national Gross Domestic Products (GDP) as well as 16% of wage employment. Moreover, agriculture earns the country 50% of revenue from exports, although it is only 15-17% of the total land in the country that has sufficient fertility and rainfall to be farmed. Over 80% of the population in Kenya depend on agriculture for their livelihood. It is also responsible for provision of raw materials for local industries, generation of employment, poverty alleviation and provision of food (Agrochemichals, 2013).

Pesticides are being used country wide for various purposes such as households, public health, the veterinary and in agricultural crop protection. Agricultural sector, however, is the most dominant consumer of pesticides in the country. Diseases and pests that affect both livestock and crops are considered the most common obstacles that reduce both quantity and quality of agricultural products. Therefore, in order to increase agricultural productivity, it is necessary to control the pests and diseases vectors using pesticides.

There are about 370 formulations registered by the Pest Products Control Board (PCPB) for use in Kenya, of which 217 are active ingredients. According to Ohayo-Mitoko, [1997] about 22% of the volume imported are classified as highly hazardous, 20% moderately hazardous, while 45% are slightly hazardous and the rest were unclassified . Different active ingredients from different types of pesticides are imported in Kenya. Annually, 7000 metric tons of pesticides are imported into the country including fungicides, insecticides, herbicides, rodenticides, fumigants, growth regulators, proteins, defoliators, surfactants as well as wetting agents (Table 1.1). According to Ngaruiya, [2004], out of the total amount pesticides imported, insecticides accounted for about 40% in terms of volume (2,900 metric tonnes) which accounted for 50% of the total cost of pesticide in 2002 .

1.8 Types and Properties of Pesticides Used in Kenya

Table 1.1. Examples of pesticides used in Kenya (PCPB 2008).

Trade name	**Active ingredients (Common name/s)**	**Manufacturer/ Registrant**	**Type**
Abalone 18 EC	Abamectin 18g/l	Agripha	Miticide
Abamite	Abamectin 20g/L	Hangzhou agrochemica ind.	miticide
Abate 500 EC	Temephose 500g/L	BASFSE	larvicide
Acanto 250 SC	Picoxystrobin 250g/Kg	Du Pont de Nemour Internationa societe	Fungicide
Acaramik 1.8 EC	Abamectin 18g/L	Rotam agrochemicals	Insecticide/miticide
Acarin T 285 EC	Dicofol 210 g/L	Syngenta crop protection	Miticide
ACE750 WSP	Acephate 750g/L	Agrolex private ltd	Insecticide
Acrobat MZ	Dimethomorph 90g/Kg Mancozeb 600g/Kg	BASF SE	Fungicide
Actara 25 WG	Thiamethoxam 250g/Kg	Syngenta	Insecticide
Actellic 25 EC	Pirimiphosmethyl 250g/L	Syngenta	Insecticide
Actril DS	Ioxynil Octanoate + 2, ester720g/L	Bayer crop science AG	Herbicide
AG Copp 75 WP	Cuprous oxide 86% w/w	American chemet corp.	Fungicide
Agil 100 EC	Propaquizafop 100g/L	Agan chemica manufacturers	Herbicide
Adonis UL	Fipronyl 12.5g/L	BASF ES	Insecticide
Agita 10 WG	Thiamethoxam 100g/Kg	Norvatis animal health inc	Insecticide
Agral 90 liquid	Synperonic NP8 900g/L	Syngenta	Fungicide
Agri-Fos 400 aq sol		Agrichem manufacturin industries	Fungicide
Agrinate 90 SP	Methomyl 90%	Vapco Ltd	Insecticide
Agristar 75 WDG	75% Tribenuronmethyl	Fluence Ltd	Herbicide
Alfatox 10 EC	Alphacypermethrin 100g/L	Sulphur mill Ltd	Insecticide
Aliette 80 WP	Fosetylaluminium 800g/Kg	Bayer crop science AG	Fungicide
Allez 200 SC	Imidacloprid 200g/L	Rotam chemicals	Insecticide

Almatix 12.5% EC	Amitraz 12.5 W/V	Makhteshim chemica works	Acaricide
Almectin 1.8% EC	Abamectin 18g/L	Denka international BV	Acaricide
Almite 2.0 EC	Abamectin 20g/L	Hangzhou agrochemica industries co. Ltd	Miticide
Alpha-aking 10 EC	Alphacypermethrin 100g/L	Gharda chemicals Ltd	Insecticide
Alto 100 SL	Cyproconazole 100g/L	Syngena crop protection AG	Fungicide
Badge EC	Bromoxynil octanoate	Amiran ltd	Herbicide
Baraki wax blocks	Difethialone	Bayer crop science AG	Rodenticide
Basagran	Bentazon	Topserve E.A Ltd	Herbicide
Basamid	Dazomet	Mura	Fumigant
Basta 20SL	Glufosinate ammonium	Bayer crop science AG	Herbicide
Basudin 600 EW	Diazinon	Ultravetis E.A	Insecticide
Battalion 2.5EC	Lamda cyhalothrin	Farmchem	Insecticide
Baycor 300EC	Bitertanol	Bayer crop science AG	Fungicide
Bayfidan 250EC	Triadimenol	Bayer crop science AG	Fungicide
Bell lindane 20 EC	Lindane	Bell industries	Insecticide
Bellamine SL	Dimethylamine salt	Bell industries	Herbicide
Bellis WG	Boscalid	Topserve E.A	Fungicide
Bellkute 30FL	Iminoctadine	Arysta lifescience corp	Fungicide
Belt 480 SC	Flubendiamide	Bayer E.A Ltd	Insecticide
Bendazim 500SC	Carbendazim	Rotam E.A	Fungicide
Bestox 20 EC	Alphacypermethrin	Juanco SPS Ltd	Insecticide
Biferan 25EC	Bifenthrin	Amiran	Insecticide
Biothane 80WP	Mancozeb	Biomedical laboratories	Fungicide
Blattanex 20EC	Propoxur	Bayer E.A	Insecticide
Bovitraz 12.5EC	Amitraz	Antipest (K) Ltd	Acaricide
Bravo 500SC	Chlorothalonil	Syngenta E.A	Fungicide
Bromatrol	Bromodiolone	Rentokil initials Kenya	Rodenticide
Buctril MC	Bromoxynil octanoate	Bayer E.A	Herbicide
Bullet 48EC	Chlorpyrifos	Orion E.A Ltd	Insecticide
Cadre	Imazapic	Topserve E.A	Herbicide
Calypso SC 480	Thiacloprid	Bayer E.A Ltd	Insecticide
Canon 5EC	Permethrin	Orion E.A	Insecticide
Captan 80WP	Captan	Arysta lifescience corp	Fungicide
Cascade	Flufenoxuron	Topserve E.A	Miticide
Celphose	Aluminium phosphide	Twiga chemicals	Insecticide
Clinic 480SL	Glyphosate isopropylamine	Anset international	Herbicide
Clortocaffar	Chlorothanil	Sipcam E.A Ltd	fungicide
Cobox	Copper	Kijani agencies	Fungicide
Coilnet	D-allethrin	Phoenix matches	Insecticide
Concord 20SL	Imidacloprid	Agriscope	Insecticide
Cyclone 505 EC	Cypermethrin	Osho chemicals	Insecticide
Cyperguard 10%EC	Cypermethrin	Twiga chemicals	Acaricide
Cypernex 5EC	Aphacypermethrin	Agrichem & tools Ltd	Insecticide
D Amine 72sl	Dimethyl amine salt	Osho chemicals	Herbicide

Daconil 720SC	Chlorothalonil	Syngenta E.A	Fungicide
Decis 0.5 ULV	Deltamethrin	Bayer E.A	Insecticide
Dipterex 2.5GR	Trichlorfon	Bayer E.A	Insecticide
Dormark 40 EW	Tetraconazole	Arysta lifescince	Fungicide
Dursban 4EC	Chlorpyrifos	Lachlan Kenya Ltd	Insecticide
Eazole 250EC	Tebuconzole	Packwell industries Ltd	Fungicide
Ectomim 100EC	Cypermrthrin	Ultravetis	Acaricide
Ectopor	Cypermethrin	Ultravetis	Insecticide
Endosulfan	Endosulfan	Bayer E.A	Insecticide
Fagilia SL	Glyphosate IPA	Bio-Medica laboratories	Herbicide
Farmcozeb 80WP	Mancozeb	Farmchem	Fungicide
Funginex 400SC	Pyrimethanil	Agrosolutions (K) Ltd	Fungicide
Gaucho 7WS	Imidacloprid	Bayer E.A	Insecticide
Glean 75 DF	Chlorsulfuron	Farmchem	Herbicide
Grenade	Cyhalothrin	Cooper Kenya Ltd	Acaricide
Herbikill	Paraquat dichloride	Osho chemicals	Herbicide
Icon 10 CS	Lambda cyhalothrin	Syngenta E.A	Insecticide
Karate	Lambda cyhalothrin	Syngenta E.A	Insecticide
Kiboko super	Fenoxaprop-P-ethyl	Amiran	Herbicide
Kocide DF	Copper hydroxide	Twiga chemicals	Fungicide
Lanirat	Bromadiolone	Ultravetis E.A	Rodenticide
Lasso GD	Alachlor	Monsanto Kenya	Herbicide
Microtech	Atrazine	NV, Antwerpen	Herbicide
Libsorb SL	Nonylphenol ethoxylate	Farmchem ltd	Surfactant
Mamba 480 SL	Glyphosate	Lachlan ltd	Herbicide
Marathon 50 EC	Malathion	Farmchem	Insecticide
Mortein doom rat kill	Brodifacoum	Reckiitt Benckiser E.A	Rodenticide
Nemathorin	Fosthiazate	Syngenta E.A	Nematicide
Orius 25 EW	Tebuconazole	Amiran	Fungicide
Palm brand	Sulphur 99%w/w	Osho chemicals	Fungicide
Polar 50%	Polyoxin AL	Amiran	Fungicide
Qamlin dust	Permethrin	Sumitomo chemicals	Insecticide
Ralon super	Fenoxaprop-P-ethyl	Bayer E.A	Herbicide
Rodazim SC	Carbendazim	Rotam E.A	Fungicide
Rugby 100ME	Cadusafos	Juanco SPS Ltd	Nematicide
Saaf WP	Carbendazim	Farmchem	Fungicide
Seed plus 30 WS	Imidacloprid	Chemturapty	Seed treatment
Sevin 85 S	Carbaryl	Antipest (K) Ltd	Insecticide
Smart fresh	Methylcyclopropene	Kakuzi ltd	Post havest treatment
Talstar 10WP	Bifenthrin	Juanco SPS ltd	Insecticide
Triatix 12.5%	Amitraz	Cooper (K) ltd	Ectoparasite
Uthane WP	Mancozeb	Dera chemical ind	Fungicide
Vegetable dust	Malathion	Aesthetics (K) ltd	Insecticide
Vydate	Oxamyl	Farmchem	Insecticide/nematicide
Wiper super 360 SL	Glyphosate	Murphy chemical (E.A)	Herbicide
Woundout 480SL	Glyphosate	Osho chemicals	Herbicide

Xentari	*Bacillus thuringiensis*	Safina E.A Ltd	Insecticide
Zaidi	Homobrassinolid	Organix Ltd	Growth regulator
Zinc phosphate	Zinc phosphate	Esam L.A Ltd	Rodenticide
Zoro TM 18EC	Abamectin	Anset international	miticide

1.9. Captafol

Captafol is a broad-spectrum protective contact fungicide. It is very effective in control of almost all fungicidal diseases of plants except powdery mildews. It is widely used outside the U.S.A to control foliage and fruit disease on citrus, apples, cranberry, tomato, coffee, potato, pineapple, onion, peanut, stone fruit, blueberry, cucumber, prune, watermelon, wheat, sweet corn, barley, oilseed rape, strawberry and leek. It is a general use sulfanimide pesticide of the isoindole family of pesticides. Captafol is a white, colorless to pale-yellow, or as a crystalline powder or solid or tan (technical grade) crystals, with a slight pungent odor. Captafol is practically insoluble in water though is soluble or slightly soluble in most organic solvents. It reacts with acid vapors, bases, acids and oxidizers [HSDB, 2010]. It hydrolyzes slowly in aqueous suspensions or emulsions, but faster in acidic and basic aqueous alkaline media [Akron, 2010]. Captafol does not burn, but emits toxic fumes such as sulfur oxide, nitrogen oxides, phosgene, and chlorine when heated to decomposition [IPCS, 1993].

The table below shows the national and regional pesticide residue limits for captafol in food.

Table 1.2. National and regional pesticide residue limits for captafol in food

Country or region limit	**Residues (mg/kg)**	**Commodities**
Argentina	10	Sour cherries
	5	Cucumber, tomato, melon, peach, water melon
	2	Plum, sweet cherry
	0.5	Grapefruit, mandarin, orange
	0.25	Apple, pear
Austria	0.1	Vegetables
Belgium	0 (0.05)	All foodstuffs of vegetable origin
Chile	15	Peaches
	10	Plums
	5	Apples, pears, tomatoes
	2	Cherries
	0.5	Carrots, onions, potatoes
	0.2	Wheat
	0.1	Carcasses (sheep, hogs, goats and cattle), milk
Czechoslovakia	15	Peaches
	5.0	Sour cherries
	2.0	Tomatoes , cherries, cucumbers, melons
Denmark	0.05	All other foods, berries and small fruits, carrots, cereals citrus fruits
European community	0.05	All products
Finland	2	Other (except cereal grains)
	0.5	Carrots, onions, potatoes
France	0.05	Cereal grains, fruits and vegetables
Germany	0.05	All food of plant origin
Hungary	15	Peaches
	10	Grapefruits, lemons, mandarins, oranges, Apples Brussels' sprouts, cabbage cauliflower, celery leaf cherries, grapes, green beans, greenhouse tomatoes green paprikas, kohlrabi, lettuce, pears, Savoy strawberries, tomatoes
	2.0	Cantaloupe, cucumbers, pumpkin, water melons, win grapes
Ireland	0.5	Beetroot, carrots, celery, horseradish, onion (green, red) parsley root, radish
Israel	0.05	All products
Italy	5	Apples, eggplant, pears
	2	Pumpkin
	0.5	Carrots, onions, potatoes
	0.1	Almonds

Japan	8 5 2 1.0 0.2 0.05	Leafy garden vegetables, tobacco Hops, other fruit and garden vegetables, apples Japanes pear, fruit Potatoes, root vegetables Cabbage, garden radish, potatoes, tea, vegetables e.t.c Cereals, sugar beets Fruit and garden vegetables
Kenya	15 10 5 2 1.0 0.5 0.2	Peaches Sour cherries Tomatoes Melons (whole), sweet cherries Cucumbers (whole) Apricots Plums
Netherlands	8 5 2 0.05 0 (0.05)	Leaf vegetables Fruit, other vegetables Root, tuber vegetables Cereals Other
Singapore	15 5	Apricots, nectarines, peaches Other fruits and vegetables
South Africa	10 5 3 0.5	Pineapples Avocados Coffee, tomatoes Potatoes
Spain	0.05	All plant products
Sweden	0.05	Cereals and hulled grains, flakes and flour made fron cereals, fruits and vegetables, potatoes
Switzerland	0.1	Cereals, potatoes
Taiwan	1.0 0.5 0.1 0.01	Berries, melons Citrus fruits, fruit vegetables, nut fruits, pome and ston fruits, tropical fruits Root vegetables Rice
United Kingdom	0.05	Apples, bananas, barley, beans, blac currants, Brussels' sprouts, cabbage, carrots, cauliflower, celery, cucumbe grapes, leeks, lettuce, maize, mushrooms, nectarines, oats, onions, oranges, othe cereals, other citrus, paddy rice, pears, peaches, peas, plums, potatoes raspberries, rye, straw berries, swedes, tomato, turnips wheat

USA	50	Sour cherries
	35	Blue berries
	30	Apricots, peaches
	15	Tomatoes
	8	Cranberries
	5	Melons
	2	Cucumbers, nectarines, peanuts (hulls), plums (fres prunes), sweet cherries
	0.5	Citrus fruits, potatoes
	0.25	Apples
	0.1	Fresh corn, macadamia nuts, nuts, onions, pineapples
	0.05	Peanuts (meats hulls removed)
	0.02	Taro (corn)
Yugoslavia	3.0	Fruits, vegetables
	0.1	Other food commodities

1.9.1 Structure:

The figure below show the structure of captafol pesticide used in this study.

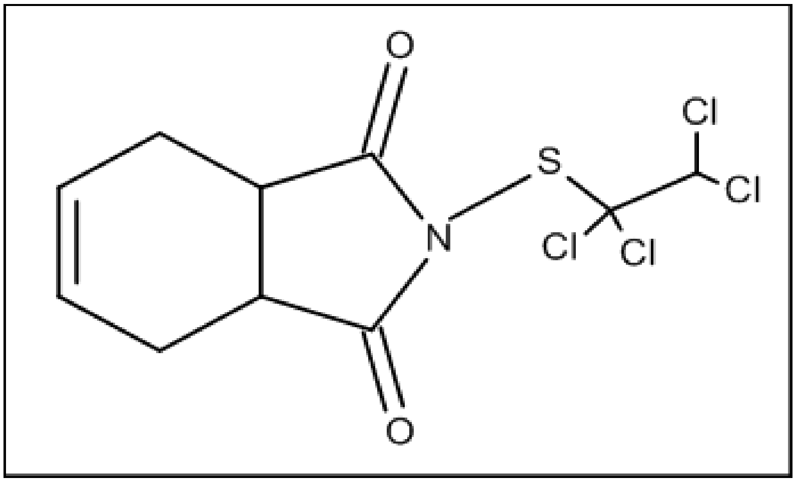

Figure 1.3: Structure of Captafol

IUPAC name: 3a, 4, 7, 7a-tetrahydoisoindole-1,3-dione;1, 1, 2, 2-tetrachloro-1-methylsulfanyl-ethane.

Molecular formula: $C_{10}H_9Cl_4NO_2S$ [RSC, 2014]

1.9.2 Properties

Molar mass: 349.06g.

Density: 1.64g/cm^3.

Melting point: 160-162 °C.

Solubility in water: 1.4 mg/L at 20°C

Solubility in other solvents (all in g/100ml): isopropyl 1.3, benzene 2.5, toulene 1.7, xylene 10.0, acetone 4.3, methyl ethyl ketone 4.4, dimethyl sulphoxide 17.0 [RSC, 2014]

1.10. Adsorption Of Captafol

Adsorption is an important factor that affects the fate of pesticides in soils. It determines their distribution in the soil or water environment. Adsorption strongly affects transport processes such as volatilization to the atmosphere, leaching into groundwater and runoff to surface water [Koskinen and Harper, 1990].

Adsorption is experienced when gas or liquid solutes accumulate on the surface of a solid. It can also occur on a liquid (adsorbent) to form a molecular or atomic film (the adsorbate) [Narayan *et. al*., 1998]. It is different from absorption whereby a substance diffuses into a liquid or solid to form a solution. The term sorption refers to both processes. On the other hand desorption is the reverse process of adsorption.

Adsorption occurs mostly in natural physical, biological, and chemical systems. This process is widely utilized in industrial applications such as activated carbon (charcoal), synthetic resins as well as water purification. Apart from adsorption, ion exchange and chromatography are the other sorption processes in which certain adsorptives are selectively transferred from the liquid phase to the surface of insoluble and rigid particles suspended in a vessel or a packed column [Benitez, 2011]. Similarly to surface tension, adsorption is as a result of surface energy. For bulky material, the bonding requirements of the constituent atoms of the material are filled up. However, atoms on the surface experiences bond deficiency, since they are not wholly surrounded by other atoms. Thus it is favourable for these materials to bond with whatever is available [Sharifah, 2006]. The ideal nature of bonding is dependent on the details of the species involved. The adsorbed material is often classified as exhibiting physisorption or chemisorption.

The amount of pesticide adsorbed in the soil depends on:

1. the type of soil
2. the soil conditions (for example temperature, moisture content and pH)
3. nature of the pesticide [Zupanc *et al.,* 2002].

Soils with high organic matter or clay adsorbs more pesticides. A pesticide adsorbed by the soil is least likely to leach, volatilize, or be degraded by microbes. However, it will be transported 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].

1.10.1 Adsorption model

1.10.1.1 Freundlich Model

The characteristic adsorption of pesticide by sediment or soils can be described by the Freundlich empirical isotherm (Graham-Bryce 1981). The adsorption kinetics of captafol onto the Ngong river sediment and soils from Kwale county will be based on the adsorption model of binary dilute solution (Burchil *et al.*, 1981)

C_{ads}=K_fCe ……………………………. (1)

Where K_f is the Freudlich constant, C_{ads} is concentration(mg/ml) of the pesticide adsorbed by the sediment/soils in a colloidal solution and Ce is the concentration of the pesticide in the solution (mg/ml) at equilibrium [Hence, 1965; Bowman and Sans, 1977.

By taking batches of known mass of sediment/ soil (adsorbent) and mixing with solution of known initial concentration of the pesticide, followed by shaking and equilibration, the concentration of the adsorbed pesticide (C_{ads}) and that at equilibrium (C_e) can be estimated. The Freudlich factor (K_f) is a constant for a given system and therefore, may be used to compare the degree of adsorption non-linearity between solution, solute concentration and adsorption [Feng and Xu, 2013].

Alot of factors need to be put into account in conducting adsorption studies. First, the kinetics involved, particularly the magnitude of the adsorption and desorption rate constant and energies involved. Second, the initial and equilibrium conditions and how the chemical composition and /or structure of both the adsorbent and the pesticide affect adsorption [Srivastava *et al.*, 2009].

In order to obtain the adsorption/desorption, equilibrium, thermodynamic and kinetic data, there is the need to come up with a functional adsorption/desorption equilibrium model from which the apparent equilibrium constant and kinetic information can be calculated. Assuming that the adsorption of pesticide solute by the colloidal/sediment or both particles occurring during the shaking period, implying that when the sediment/soil is in suspension, then the adsorption/desorption equilibrium can be described as follows [Seungman *et al.*, 2005].

$nX+S\leftrightarrow SXn$ ……………………………………..(2)

$K=[SX_n]/[X]^n[S]$…………………………………….(3)

On re-arranginging,

$[SX_n]=K[X]^n[S]$ ……………………...…………….(4)

Where X is the pesticide molecule of interest, S is adsorbent/substrate and K is the adsorption/desorption equilibrium constant. SXn is the particle-pesticide adsorption complex. S is a solid whose mass is large compared to that of the solute. Therefore, [S] can be taken to be unity thus reducing equation (4) to:

$[SXn]=K[X]_n$ ……………………………………….(5)

Taking the logs we have;

$\log [SX_n]=\log K+n\log[X]$ …………………………….(6)

Since the equation (6) is linear, the value of K (equilibrium constant), n (the number of pesticide molecules adsorbed) can be obtained from the slope and intercept of log $[SX_n]$ versus log[X] respectively. In addition, the standard Gibbs free energy of activation, ΔG, can be estimated by the use of conventional equation below.

$K= e^{-\Delta G/RT}$ … ……………………………………….. (7)

When the assumption that adsorption of diquat pesticide by sediment/soils occur while shaking, and also that the adsorbed pesticide goes to the sediment on settling, then the concentration of the pesticide adsorbed to the suspended particles $[X]_{ads}$ can be obtained using the equation below.

$[X]_{ads} =[X]_i-[X]_e$

Where $[X]_i$ represents the initial pesticide concentration before a known mass of sediment/soil is added and $[X]_e$ represents the equilibrium pesticide concentration. Agitation facilitates the settling down of the sediment/soil and thus separation of dissolved and adsorbed pesticide. Since *n* molecules of the pesticide are associated with a single adsorption site, then $[SX_n]$ is given by:

$[SXn]=1/n\ ([X]_i–[X]_e)$…………………………….(9)

$[SXn]=1/n[X]_{ads}$ ………………………………… (10)

Nomura and Hilton [1977] and later Zaranyika *et al.* [1993] demonstrated the existence of a colloidal bound fraction when a pesticide is shaken with water containing sediment.

On modifying equation (10), the total adsorbed pesticide is given by the following equation 11.

$[X]_{ads}=nK'\ ([X]e + [SXn]w)$…………………….(11)

Where K' is the apparent adsorption equilibrium constant and [SXn]w is the concentration of the colloidal bound fraction in suspension at settling equilibrium. On taking the natural logarithm of equation (11) yields a linear expression is obtained;

$\ln[X]_{ads}=\ln\ (nK')+n\ \ln([X]e +[SXn]w)$ ……….(12)

Assuming that equilibrium exists between the colloidal bound fraction in the sediment/soil and that in the suspension, then equation (2) becomes:

$nX+S\leftrightarrow (SXn)w\leftrightarrow(SXn)sed/soil$ ……………….(13)

It is, therefore, apparent from equation (13) that the steady state exist with respect to [SXn]w at settling equilibrium. A plot of $\ln[X]_{ads}$ versus $\ln\ ([X]_e + [SX_n]w)$ in equation (12) will not affect the value of n in equation (6) and (10) but will affect the value of nK. Therefore, the value of K obtained is not a true equilibrium constant but an apparent equilibrium constant (K').

1.10.1.2 Langmuir Isotherm

Irving Langmuir in 1916 published a new isotherm for gases adsorbed on solids and was later named after him. The empirical isotherm is derived from a proposed kinetic mechanism. The basis is on four hypotheses:

1. Adsorbed molecules do not interact.

2. The adsorbent surface is uniform, that is, all the adsorption sites are equal.

3. A monolayer is formed at the maximum adsorption: 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 rarely 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.

4. All adsorption occurs through the same mechanism.

The third condition is the most troublesome since more molecules can adsorb on the monolayer, but this problem is solved by the BET isotherm [Obayashi *et al.,* 2003].

The Langmuir equation is expressed as [Young and Crowell, 1962]:

$x/m = q_{max}\ bq_e / 1+bq_e$

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 a 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).

Either of these equations may be used to evaluate b and qmax from experimental data using graphic or linear least square analysis [Rubin and Mercer, 1981].

1.11 objectives

1.11.1 overall objectives

To determine the existence of adsorption/desorption equilibrium of captafol pesticide by sediment from Ngong river and kwale red soil samples.

1.11.2 specific objectives

1) Establish the characteristics of captafol using UV-VIS-NIR spectrophotometry technique.
2) Investigate the effects of different concentrations of pesticide and the effect of different shaking time on adsorption.
3) Determine the thermodynamic properties of captafol -water-soil systems i.e. n, ΔG and K’.
4) Compare selected physical properties of the sediment and soil samples and determine their relationship to the thermodynamic properties

1.12 Problem statement

Pesticides are currently used by farmers as an effective control against most weeds and unwanted growth of vegetation in the farms. These pesticides may be extremely hazardous if not properly used. Some of the pesticides are carried to water bodies through run-off. It is not clear from literature how much of this pesticide is retained by the soil after its application. The retained pesticide may cause future harm to plants grown in the same land or can cause poisoning in water bodies that are deposited in. Therefore, there is need to establish the proportion of pesticide that is discharged to the environment and how much can be adsorbed by different soils.

1.13 Justification

The working model is to estimate how much of captafol pesticide could be adsorbed onto the soil and sediment in the environment. It is not clear from the literature on how much of this pesticide is adsorbed in the environment. Pesticide sorption affects other processes like transport, degradation and bioaccumulation among others which influence the final fate of these compounds in the environment (Gao *et al*., 1998). The knowledge of pesticide adsorption characteristics of the soil is vital for predicting their mobility and fate in the environment.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Environmental pollution from agricultural chemicals

Environmental pollution from agricultural chemicals is of growing concern today due to the excessive use of pesticide chemicals. Once the chemical reached the soil, it is subjected to different physicochemical interactions of which adsorption-desorption characteristics are the most important [Weber *et al*., 1991]. This chapter gives a review of various factors that influence the adsorption-desorption in soil.

2.2 Soil constituents

A typical soil environment contains solid, liquid and gaseous phases [Hamaker and Thompson, 1972]. For the adsorption and desorption of organic chemicals, the features of the solid phase are the most important. The major adsorbing surfaces in soil are clays, organic matter (OM) and amorphous minerals [Wu *et al*., 1975; Moll *et al*., 1982]. As clay and OM in soils do not exist as separate entities, it is often not possible to know which soil component is involved in the sorption process [liger and Yaron, 1975]. Clays represent layers of silica and aluminum sheets, each silica sheet consist of a silicon atom which is surrounded by four oxygen atoms in a tetrahedral symmetry. On the other hand, the alumina sheet has aluminum atoms coordinated by six oxygen or hydroxyl groups in an octahedral fashion. Isomorphic substitution of $\mathrm{AI}^{+}\mathrm{Fe}^{+}$ for Si^{+} in the tetrahedral layer, and Mi^{+} for AI^{+} in the octahedral layer produce a change in the net charge on the surface, the generated negative charge being responsible for organic chemical adsorption. Clays are characterized by properties such as lattice expansion, cation exchange capacity (CEC) and surface area. The typical surface area of clays is between 600 and 800 $\mu m^2/g$. Adsorption of organic chemicals by clays offers room other soil components because of CEC, strength of the negative charge, specificity of adsorption sites and the nature of the cation on the exchange complex [Calvet, 1980].

Soil organic matter is formed by the degradation of plant and animal tissues. The major constituents of OM are polymeric organic acids, which are mainly humic acid, fulvic acid and humin. OM is by its solubility in alkali or an acid. The acid component of OM is due to fulvic acid, whereas the alkali component is humic acid. Humin is the insoluble component. Soil OM also possesses a large surface area (50-80 $\mu m^2/g$) and its cation exchange capacity is in the range of 20-40 meq/10 g. Large surface area and the presence of different functional groups are responsible for high adsorption capacity [Haque, 1974]. The adsorption of organic chemicals onto OM varies from soil to soil due to the differences in composition, presence of different functional groups and the degree of cation saturation [Morrill *et al*., 1982].

Amorphous mineral colloids are oxides of aluminum, silicon and iron. These are induced by the weathering of soil minerals, often serving as cementing agents [Wada and Haward, 1974]. Amorphous materials are amphoteric in nature and their reactivity is strongly influenced by pH [Morrill *et al*., 1982]. Presence of Al and Fe in amorphous minerals can influence organic chemical behavior by acting as exchangeable ions on the exchange complex [Adams, 1972]. The CEC of amorphous minerals varies from 5 to 30 meq/10 g and is responsible for most of the anion adsorption in soils. The surface area of amorphous minerals is in the range of 10-80 $\mu m^2/g$ [Morrill *et al*., 1982].

2.3 Adsorption-Desorption Characteristics

The literature on sorption of organic chemicals in soil and on soil components is voluminous. Literature citations in this study are limited to research that appear to be significant in natural soil systems, recognizing the complexity of soil-solute interactions.

2.3.1 Adsorption

Adsorption may be as the spontaneous deposition of a solute onto a solid surface resulting from the interaction between the fields of force of the sorbent and the molecules or ions of the adsorbate [Rao, 1990]. It is either positive (favorable) or negative (unfavorable) depending on whether the adsorbate is attracted or repelled by the adsorbent. Positive adsorption from a solution occurs when there is an attraction between the adsorbate and the adsorbent resulting in higher concentration of adsorbate at the liquid-solid interface than in bulk solution. Negative adsorption occurs when there is a higher adsorbate concentration in the bulk solution than at the liquid-solid interface [Hamaker and Thompson, 1972].

The adsorption process of organic chemicals including phenoxy acetic acids and chlorophenols onto soils and sediments has been critically evaluated and summarized in several review articles [Hamaker and Thompson, 1972; Calvet, 1980; Karickhoff, 1981, 1984; Morrill *et al.*, 1982; Rao *et al.*, 1982; Chiou, 1989; Weber *et al.*, 1991]. The major factors influencing adsorption are: physical and chemical characteristics of the soil constituents whih include:

1. pH, % organic carbon (OC), clay fraction, surface area, and surface charge; nature of the organic chemical.

2. Ionization constant (p.), solubility, charge on the molecule, molecular size and polarity and

3. pH and temperature of the system.

The prevailing hypothesis is that, for sorption of nonionic organic chemicals, organic matter is the dominant sorbent. Sorption is envisioned as a partitioning process, in which the sorbate permeates into the organic matter. The majority of the reported studies [Kirchhoff, 1981; Chiou, 1989; Che *et al*., 1992; Haderlein and Schwenbach, 1993; Dell *et al*., 1994; and Kan *et al*., 1994] on organic chemical sorption onto soils were done at low concentrations. The important conclusions from these investigations are:

1. Linear sorption isotherms over a considerable concentration range was observed

2. Existence of an inverse, linear relationship between solute aqueous solubility and adsorption capacity;

3. Low heats of adsorption (4-7 kcal/mol); and

4. Absence of competitive sorption when solutes are present as mixtures.

The adsorption of phenoxy acetic acids, 2,4-D, 2,4,5-T and MCPA, on clay materials, was investigated by Frissel (1961), Weber et al. (1965), Bailey et al. (1968) and others. Bailey et al. [1968] found no significant adsorption of phenoxy acetic acids by montmorillonite clay at high pH values. The authors also report that positive adsorption of these acids occurs when the pH is below the dissociation constant (pK) of the acids, i.e., when compounds re in molecular form.

Harris and Warren [1994] examined the adsorption of 2,4-D and other herbicides in relation to pH, temperate, and the nature of the adsorbent. All herbicides investigated by them showed increased adsorption at low pH values. Also, organic soil was found to adsorb more in comparison to a clay soil. The adsorptive behavior of 2, 4-D onto various synthetically prepared organo-clay complexes, which are similar to naturally occurring organo-complexes of soil, was investigated by Miller and Faust [1972] and Kahn [1974]. Khan [1974] reports that the adsorption of 2, 4-D onto these complexes is higher than onto clays. Similar results were obtained by Miller and Faust [1972]. The adsorption of 2, 4, 5-T onto four different soils was examined by O'Connor and Anderson [1974]. Their results indicated that when 2, 4, 5-T is adsorbed to the organic matter in the soil, adsorption capacity increased with increasing organic matter content.

The adsorption of 2, 4-D and some other selected herbicide chemicals, at high concentration were investigated by Rao and Davidson (1979) on three different soils. They concluded that Freundlich-type isotherms describe pesticide adsorption over the concentration range, and the adsorption isotherms are favorable and nonlinear. The uptake of 2,4-D onto Ohakea silt loam is described by the Freundlich isotherm (Bhamiimri and Perrie, 1992). Mallawatni and Mulla (1992) reported similar results for 2, 4-D adsorption onto Naff silt loam.

The sorption studies of chlorophenols onto soils are limited. Boyd [1982] investigated the adsorption of chlorophenols including 2, 4-DCP and 2,4,5-TCP, the results indicating that the adsorption capacity increased as the number of chlorine atoms increased on the molecule. Schellenerg *et al.* [1984] found that the sorption of chlorophenols by sediments and aquifer materials is due to solute partitioning. The resulting isotherms were linear over a wide range of solute concentrations and dependent on the soil organic matter. The adsorption of PCOC onto Ohakea silt loam is described by a nonlinear Freundlich type isotherm [Bhamidimarri and Perrie, 1992]. Bellin *et al.* [1990] reports that the adsorption of pentachlorophenol (PCP) onto soil follows Freundlich isotherm.

While several researchers have investigated studies on the competitive sorption of organic chemicals onto soils, their results have shown no competition for nonionic solutes [Krickhoff *et al.*, 1979; Chiou *et al*., 1983]. However, some researchers report relatively small decreases in sorption resulting from competition [McGinley *et al*., 1993]. The sorption of trichloroethene (TCE) and p-xylene from single and bicomponent solutions by two aquifer materials was examined by Lee et al. (1988). They observed no difference in sorption between the single and binary systems. The sorption of trichloroethylene by a sandy aquifer material in single and ternary-solute systems is the same [Busseau and Rao, 1991].

2.3.2 Desorption

The reversibility of the sorption process plays a significant role in determining the behavior and fate of organic chemical in the soil, that is, whether the chemical is adsorbed permanently onto the solid phase or released back into solution in a reaction to a decrease in solution concentration.

Studies of solute desorption from soils are scarce and inconclusive [Voice and Weber, 1983]. Desorption experiments are done with adsorption studies to determine the reversibility of freshly adsorbed compounds onto soil matrix. However, in many instances the time frame and conditions usually encountered in the field are difficult to simulate in the laboratory. In modeling solute transport, the adsorption/desorption process is often simplified by assuming ideal conditions of instantaneous equilibrium, isotherm linearity and desorption reversibility [Brusseau and Rao, 1989]. However, considerable field and laboratory data deviate from that predicted by this simple model approach. As a result, the assumption of ideal behavior has been challenged by many researchers [Ball and Roberts, 1991; Pavlostathis and Jaglal, 1991].

Adsorption/desorption behavior of a solute which does not conform to the ideal conditions has been attributed to many different factors, including the following:

1. Varying adsorption energies, leading to isotherm nonlinearity, i.e., a Freundlich type isotherm [Busseau and Rao, 1989];

2. Failure to attain equilibrium in either the adsorption or the desorption directions due to slow kinetics in either step [Wu and Gschwend, 1986];

3. Chemisorption of the solutes to various components of the soil matrix, leading to irreversible adsorption [Brusseau and Rao, 1989];

4. Either biotic or abiotic degradation of the solute being studied, causing an apparent irreversible adsorption [Mller and Pedit, 1992];

5. Adsorption/desorption hysteresis [Busseau and Rao, 1989]; and

6. Experimental procedures, such as centrifugation versus dilution [Bowman and Sans, 1985].

Harris and Warren [1994] studied the desorption of 2,4-D from muck soil and report that successive extractions with distilled water desorbed only half of the initially adsorbed 2,4-D; the concentrations of the herbicide in the final extracts are extremely low. Van Genuchten *et al.* [1974] and O'Connor *et al.* [1980] investigated the adsorption and desorption characteristics of 2, 4, 5-T on Glendale clay loam and observed that the adsorption and desorption isotherms are different depending on the amount adsorbed onto the soil at equilibrium. Krickhoff and Morris [1985] studied the long-tem desorption of organic contaminants, reporting that the last portion of the sorbed material (10% of the initial sorbed mass) tended to desorb very slowly.

Che *et al*. [1992] examined the desorption of the herbicides, imazaquin and imazethapyr from clay and found that most of desorption occurred on the first cycle, with100% of the adsorbed herbicide desorbed after five desorption cycles. Bhamidimari and Petrie [1992] reported that the desorption of 2, 4-D and PCOC from Ohakea silt loam is 82 and 84%, respectively, the desorption of the compounds was found to be a function of the amount of solute adsorbed onto the soil. Chen and

Maier [1992] observed that only 15% of phenanthrene is desorbed after first re-equilibration; after 7 days, 55% of the total adsorbed could be desorbed.

Grathwohl and Reinherd [1993] examined the desorption behavior of TCE onto aquifer materials for different time scales. When the equilibration time is short (23 min) 96% of the adsorbed solute was removed from the soil. However, when the equilibration time is longer than 5 days, only 73%of the TCE was desorbed. When desorption of naphthalene from a contaminated soil wasexamined, Connaughton *et al*. [1993] report that 70-80% of the sorbed naphthalene could be easily desorbed, the remainder showing increased resistance to desorption.

2.3.3 Hysteresis

Hysteresis is when for a given equilibrium concentration solution, more chemical is retained on the soil during the desorption phase than the adsorption phase. The concept and existence of true hysteresis in adsorption and desorption is well [Brusseau and Rao, 1989; Adamson, 1990]. Adamson [1990] suggests that there are three major types of hysteresis loop shapes: two types of closed-loop hysteresis where desorption is 10% complete and one type where a reaction of the solute is irreversibly bound to the adsorbent (even at zero solution-phase concentration). While most of these observations are based upon the adsorption of gases onto different solids, the same arguments re extended to the adsorption of organic solutes from aqueous solution onto porous adsorbents [Kan *et al*., 1994].

Kan *et al*. [1994] suggested that the open-loop hysteresis, observed in soil-solute systems, is probably due to mechanical or structural rearrangement of the adsorbent, i.e., the solid from which desorption takes place is different from that during adsorption. This hysteresis is termed as irreversible adsorption. Based on experimental results, Kan *et al*. [1994] suggests three types of anomalous adsorption /desorption behavior: apparent hysteresis, which is the result of some experimental artifact; true hysteresis, which is time invariant and repeatable; and irreversible adsorption, which is associated with some rather permanent change on the adsorbent/adsorbate system.

Swanson and Dutt [1973] and Honsby and Davidson [1973] were the first to report hysteresis in soil systems. Hysteresis in sorption isotherms of hexachlorobiphenyl on sediments is observed by Horzempa and Di Toro [1983]. A number of studies show that the reaction of the sorbed solute at the end of the adsorption cycle is difficult to remove after several desorption steps, attributing this to hysteresis in adsorption-desorption [Swanson and Dutt, 1973; Rao and Davidson, 1980]. Pavlostathis and Jaglal [1991] also observed hysteresis in the adsorption and desorption of TCE from silty clay. Recently, Kan *et al*. [1994] reports hysteresis in adsorption and desorption behavior of naphthalene, phenanthrene and p-dichlorobenzene from soils and sediments.

2.3.4 Effect of Temperature

Generallry, adsorption processes are exothermic, while desorption processes are endothermic [Rao, 1990]. This variation of temperature affects surface-solute, and water-solute interactions, the balance between the two effects resulting in adsorption increasing, decreasing or remaining unaffected [Calvet, 1980]. In general, for neutral organic compounds, the isosteric heats of adsorption (ΔH), which measure the strength of sorption, are relatively low; increased sorption capacity is not with comparable increases in ΔH [Chiou *et al*., 1979].

Harris and Warren [1994] studied the effect of temperature on the adsorption of 2,4-D by clays and a muck soil and found that the adsorption of 2,4-D by bentonite is greater at 0 ºC than at 50 ºC , while in muck soil (high organic matter soil) the extent of adsorption at 0 ºC and 50 ºC is similar. The authors attribute this lack of a temperature dependence for muck soil to its ion-exchange mechanism. Khan [1973, 1974] also examined the adsorption of 2,4-D at two different temperatures onto organo-clay complexes and reports that the adsorption capacity decreased as the temperature was increased from 5 to 25 °C. The above results indicate that the sorption capacity is influenced by temperature.

On the other hand, the sorption of nonpolar organics was found to be independent of temperature [Chiou *et al*., 1979; Hassett *et a*l., 1980]. While these authors have obtained identical isotherms and constants at 15, 25 and 35 °C for this class of compounds, the lack of a temperature dependence is attributed to similar enthalpies of the solutes in solution and the organic phases of soil [Chiou *et al*., 1979]. Nonpolar organic solutes form weak van der Waal bonds with the solvent (water) as well as with the sorbent - hence the sorption is independent of temperature [Hassett *et al*., 1983].

2.3.5 Effect of pH

The acidity of an adsorbent system is measured by the pH of the solution in contact with the solid phase. Calvet [1980] found the pH of the solution has a marked effect on adsorption of organic chemicals onto soil. Reporting three variations of adsorption: adsorption of weak bases on negatively charged adsorbents - clays, humic acids; adsorption of weak acids on positively charged adsorbents - oxides and hydroxides; and adsorption of neutral molecules on clays and soils.

The essential feature of weak acids and weak bases is that they exist as ions or neutral molecules depending on solution pH. Weak acids are in molecular form at low solution pH, whereas weak bases are converted to cations at low pH [Hamaker and Thompson, 1972]. The degree of association or dissociation of organic chemical is a function of its pKa. A compound, when present in molecular form or ionic form, affects the extent and magnitude of adsorption and the strength by which it is, because the adsorption can be different between the associated and dissociated forms [Hermosin and Cornejo, 1993].

The influence of pH on phenoxy acetic acids adsorption onto clays was studied by several researchers [Bailey *et al*., 1968; Hermosin and Cornejo, 1993]. These authors report that the positive adsorption of phenoxy acetic acids occur when the pH of the solution is near or below the pH of the compound. Fontaine *et al*. [1991] observed a clear trend of increasing sorption with decreasing pH for the acid herbicide, flumetsulam. Authors attributed this to theexistence of a large proportion of neutral molecules at low pH values. Also, the flumetsulam sorbs to the soil more strongly than the anionic form. The pH dependence of adsorption has been reported for other acid herbicides [Walker *et al*., 1989; Stougaard *et al*., 1 990]. Che *et al.* [1992] evaluated the effect of pH on adsorption for two herbicides and observed that sorption increased as pH decreased. The amount of 2,4-D adsorbed onto clays decreased continuously when pH increased from 0.7 to 8 [Hermosin and Cornejo, 1993].

Hassett and Banwart [1989] investigated the adsorption of chlorophenols on soils and report that chlorophenols are adsorbed below their pH values. For chlorophenols with low pH values, especially PCP, the overall uptake at normal soil pH is relatively low because a high fraction of the compound is ionized. The sorption of pentachlorophenol is shown to depend on the proportion of anion to neutral forms [Lee *et al*., 1990].

Haderlein and Schwarzenbach [1993] report that the sorption of nitrophenols onto kaolinites is strongly influenced by the solution pH with maximum sorption occurring below the pH value of the respective compounds.

The observed increase in adsorption capacity at low pH is explained by the effects of hydrogen ions on solute and the adsorbent Protons cause conformational modification of humic substances and hydrolyze the clay lattices. Hydrolysis of clays brings Al^{+3} and Fe^{+3} ions to the surfaces, which are more or less covered by hydroxides. These compounds are highly adsorbent and frequently responsible for observed increases in adsorption at low pH [Calvet, 1980]. When adsorption is at maximum, the corresponding pH is sometimes the pKa value. This is not always the case as it is sometimes coincidental.

2.3.6 Adsorption Mechanisms

Sorption processes are by a variety of forces and/or mechanisms affecting the relative bonding of the solute and sorbent versus the solvent and solute [Hassett and Banwart, 1989]. The mechanisms and bond energies of organic chemicals adsorption onto soils are listed in Table 2. 1

Table 2.1: Bonding mechanisms of organic chemicals in soils (Morrill et al., 1982).

Mechanism	**Reported Bonding Energy (Kcal/Mole)**	**Chemical Types**
Hydrogen bonding	0.5-15	Carbonyls, aliphatic amines, chlorophenols
Van der Waals	1-2	Larger molecules: 2,4-D on OM, picloram, linuron
Coordination	-	Amitrol, urea, amino acid, alcohols
Ion exchange	up to 50	Amines, acids and /or ionized bases, hydroxides sulfonate and sulphite surfactants.
Chemisorption	30-190	Amines and pyridines on Mg- and Ca saturated clays

Physical adsorption results from electrostatic interactions between atoms, ions and molecules due to the electron fluctuations producing instantaneous dipoles. The van der Waals interactions re weak and decrease rapidly with the distance between the interacting species. Examples of physical adsorption are linuron and 2, 4-D on humic acids [Morrill *et al*., 1982].

Hydrogen bonding is a partial charge transfer interaction in which the hydrogen atom serves as a bridge between two electronegative atoms, one held by covalent bond, the other by electrostatic forces [Hadzi *et al*., 1968]. The presence of oxygen-containing functional groups and amino groups on organic matter indicates that the adsorption could occur by the formation of a hydrogen bond with the organic chemicals containing similar groups [Morrill *et al*., 1982]. The energy of desorption in hydrogen bonding varies from 0.5 to 15 kcal/mol. The adsorption of 2, 4-D on clays (e.g., montmorillonite) involves hydrogen bonding of the CO group to the hydroxyls of the clay surface [Hermosin and Cornejo, 1993].

Ion (cation/anion) exchange is a process in which one ion is from a solution in exchange of another type present on the soil. The columbic forces of attraction are very large (50 kcal/mole). When organic molecules become positive by protonation (amine, alcohol, carbonyl groups), ions are adsorbed on clay depending on the CEC of the clay minerals. Protonated forms of atrazine and prometryn are adsorbed on clay complexes by ion exchange mechanism [Morrill *et al.,* 1982]. Anion exchange reactions are not as cation exchange reactions in soils, in general, anions are adsorbed either electrostatically or with a degree of chemical bonding by soils [Hassett and Banwart, 1989].

Coordination is an important mechanism in the adsorption of nonionic polar molecules. The coordination complexes are by the donation of electron pairs by the ligand and the acceptance by the metal resulting in the filling or partial filling of orbitals. Khan [1974] reports that the adsorption of linuron on montmorillonite is due to coordinate bonding. In chemisorption, electrons are redistributed in new orbitals and a permanent chemical bond. Chemisorption is exothermic with an energy range of 30- 190 kcal/mole [Calvet, 1980]. The adsorption of nemagon on illites is due to chemisorptions [Morrill *et al.,* 1982]. Hydrophobic sorption is due to partitioning of the nonpolar organic from the polar aqueous phase into hydrophobic surfaces in the soil [Hassett and Banwart, 1989]. A feature of hydrophobic bonding is the weak interaction between the solute and the solvent. The primary force in the hydrophobic sorption appears to be the large entropy change resulting from the removal of the solute from the solution. The adsorption of a number of nonpolar organic chemicals is due to the hydrophobic sorption [Chiou *et al*., 1979; Chiou, 1989]. The two important mechanisms by which phenoxy acetic acids and chlorophenols adsorb onto soils are hydrogen bonding and physical adsorption [Boyd *et al*., 1989; Hermosin and Cornejo, 1993].

CHAPTER THREE

3.0 METHODOLOGY

3.1 Instrumentation

The instrument/equipment used for the current study were; UV-Vis-NIR spectrophotometer (Shimadzu 3700PC); pH meter (3520 model); Orbital shaker (Fischer scientific A-160); Oven and Analytical balance.

3.2 Chemicals

All chemicals used were analytical grade. Captafol was obtained from Kenya bureua of standards (KEBS). Captafol used was 99.7% pure and the reagents were analytical grade.

3.3 Reaction Vessels

Pyrex conical flasks and glass vials were used in this study. The vessels were washed thoroughly with perchloric acid then rinsed with distilled water and dried at 110 ^{o}C for 0.5 hour prior to use in a glassware oven.

3.4 Captafol Standard Solutions

A stock 100 ppm solution of captafol was prepared by transferring exactly 0.2875 mL of (0.350 g/mL) solution of captafol into a 100 ml volumetric flask. The volume was diluted to the mark with Acetonitrile:water solution (70 : 30 % v/v).

3.5 Soil Sampling

The red soil used in this study was collected from Kwale county while the sediment was collected from Ngong river in Nairobi. The collected soil samples were stored in a plastic bag and frozen during transit.

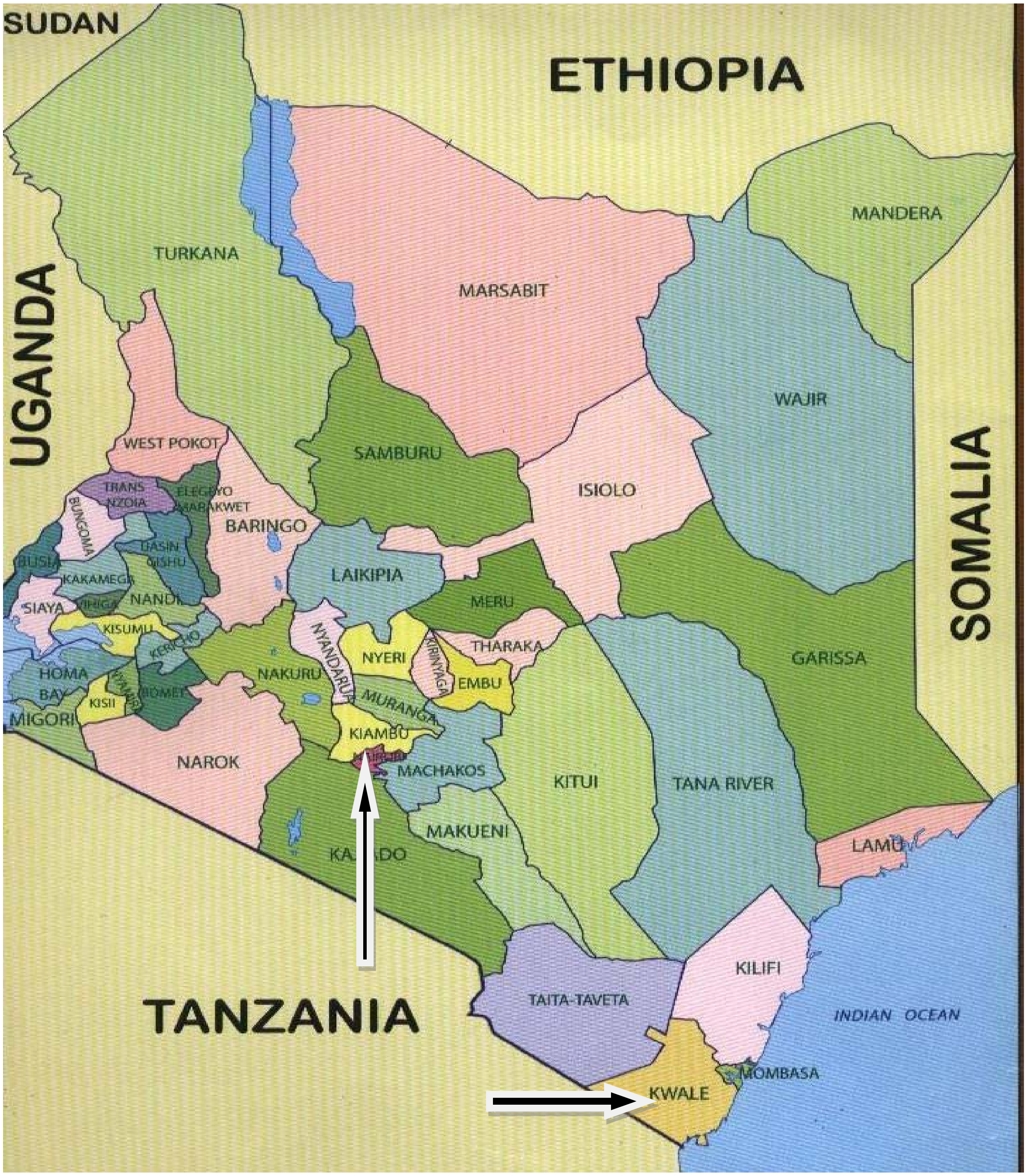

Figure 3.1: Map of Kenya showing counties where sample were collected.

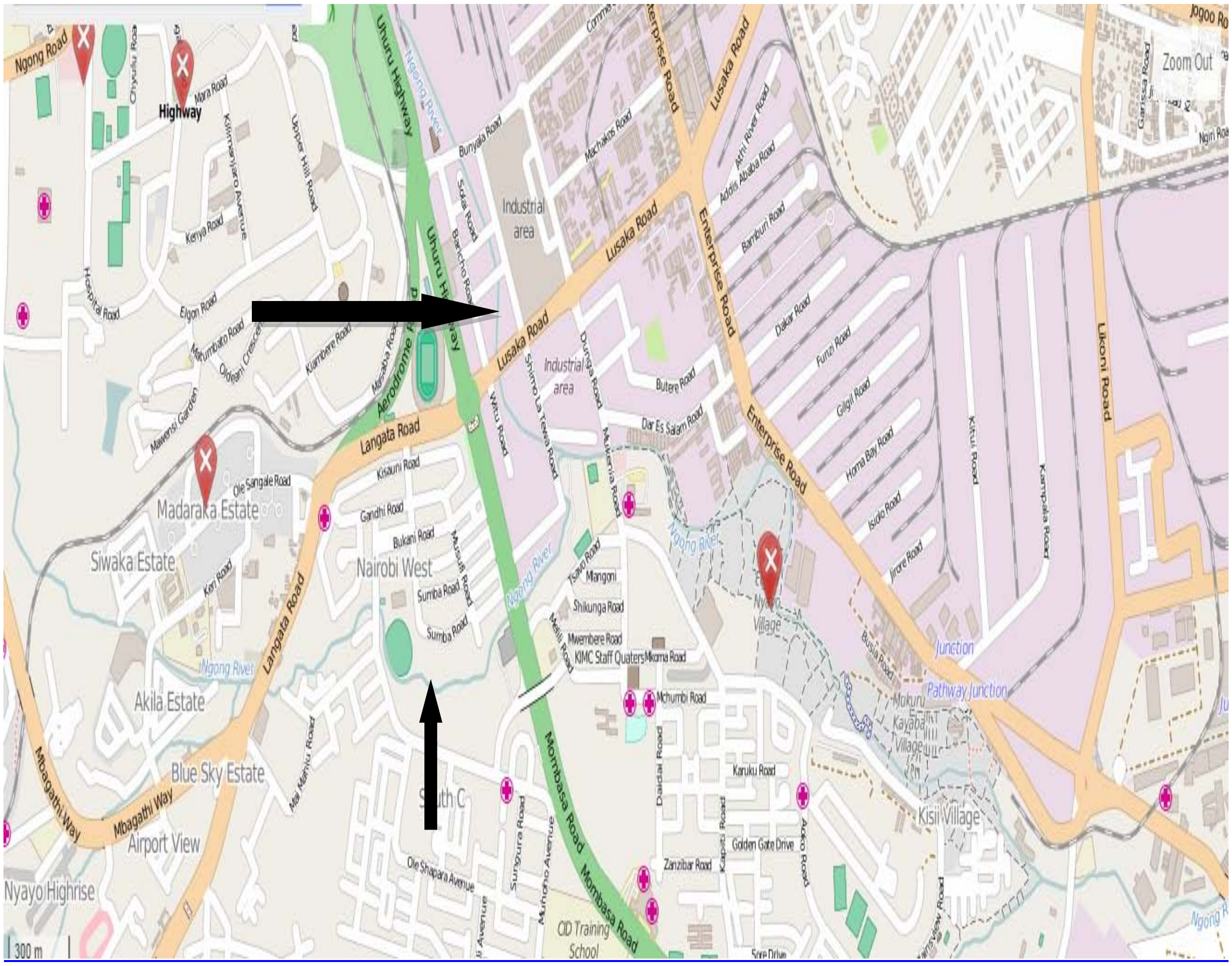

Figure 3.2: Map showing Ngong River (Open source map, 2015).

Soil pH was determined by using a direct reading type pH meter with glass electrode and calomel reference electrode. The soils were sieved through IS (International Standard) sieve No. 10 (2 mm 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.

3.5.1 Soil Characteristics

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

3.5.1.1 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 for about 1 minute. After 30 minutes 100 mL of distilled water and 0.30 mL of 0.025 M ortho-phenanthrolin- 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, 1998).

The following equation used to calculate the T.O.M %: Organic carbon (%) = ((5m_{eq} $FeSO_4$) x 0.399)blank) / sample dry weight (g) and T.O.M % =1.27 x organic carbon %.

3.6 Adsorption Study

3.6.1 Kinetic Study

The adsorption kinetic study was carried out in batch mode using 10 ml vials with 0.5 g of appropriate soil/sediment, with a solid: solution mass ratio of (1:20) and 10 ml of 100 ppm of technical captafol solution. Sorbent masses were accurate to ± 0.001g and solution volumes to ± 0.5 ml. The studies were conducted in triplicate for all samples on an orbital shaker (Fischer scientific A-160) at 150 revolutions per minute (rpm) for a period of 24 h at room temperature (25 ± 2 °C). From the triplicate flasks, 5 ml of sample was collected at time intervals of 0.5, 1, 2, 3, 8 and 24 h. The collected samples were filtrated and analyzed by theUV-Visible-NIR spectrophotometer.

3.6.2. Equilibrium Study

Adsorption equilibrium studies were conducted for all soils with an adsorbent quantity of 5 g with technical captafol concentrations of 50, 60, 70, 80, 90 and 100 ppm in identical vials containing 10 ml of distilled water. A blank was maintained to determine the effect of captafol adsorption on the vials. 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 ± 2 ^{o}C. After 3 h, 5 mL of sample was collected from each vial, the collected samples were filtrated and analyzed using UV-Visible-NIR Spectrophotometer.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Calibration graph

Standard solutions of captafol 1, 2, 4, 6, 8, 10, 20, 40, 60, 80 and 100 ppm were prepared by serial dilution from the 100 ppm standard stock solution of captafol into 5 ml volumetric flasks and diluting to the mark with ethanol :water solution (70:30% v/v). The absorbances were measured at 420 nm (Verma et al.,1991) against a blank solution. The following figure 4.1 shows the spectra of captafol in ethanol.

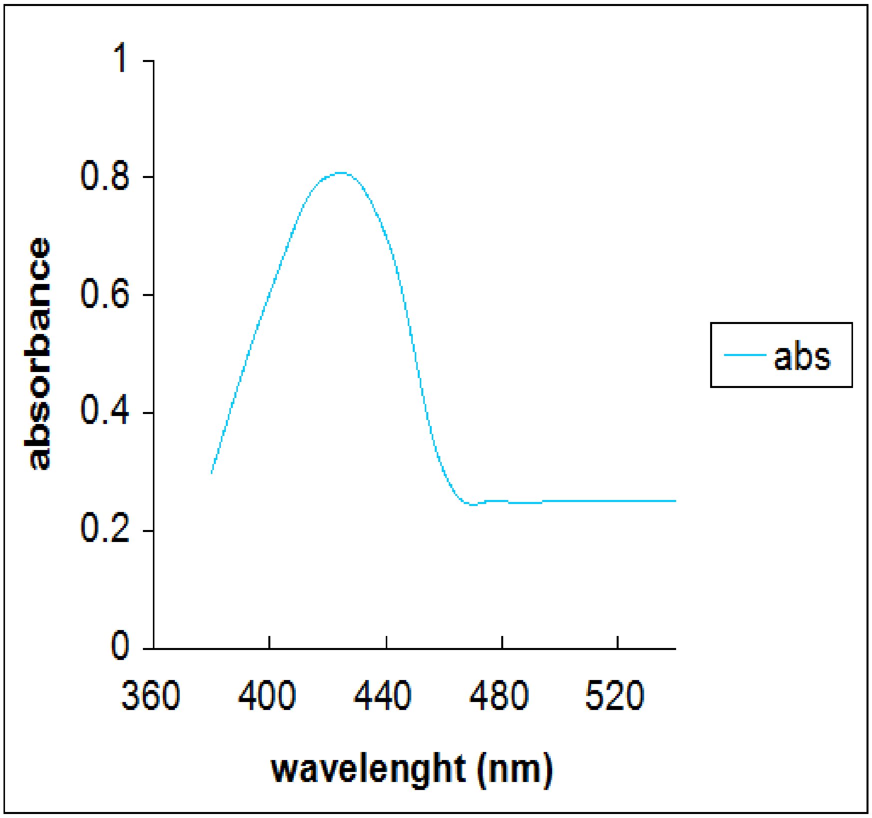

Figure 4.1. Captafol spectra in ethanol.

A linear relationship was obtained between the absorbance and the concentration of captafol within the range of 0-100 ppm. From the calibration curve (Fig. 4.2) the detection limit was found to be

0.001 ppm. In figure 4.2 below, a linear range was observed with concentration range of 0-20 ppm. Thereafter was a slight deviation as the concentration increased from 20 to 100 ppm. This was in accordance with Beer-Lambert's law. The calculated morlar absorptivity for captafol was 0.006709 L mol^{-1}cm^{-1}.

The calibration curve for captafol is shown in Figure 4.2.

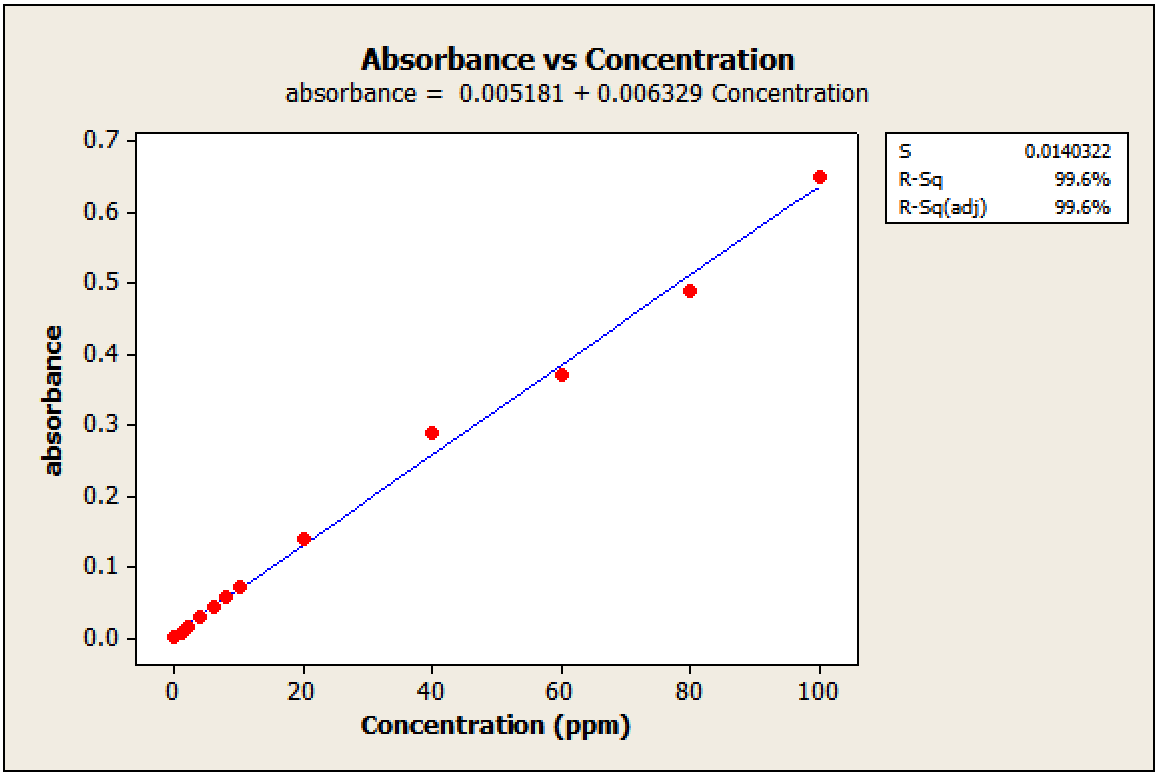

Figure 4.2. Calibration curve for captafol.

From figure 4.2 above shows that the data fitted very well in the plot. This is signified by the high value of correlation coefficient (R-Sq) of 0.996. The adjusted regression coefficient (R-Sq adj) of 0.996 which is the same as the regression coefficient means that the data has not been modified. The S variable is the standard error of the regression. From the above graph, the error (0.014) is so small and therefore the results obtained were precise.

4.2. Adsorption

4.2.1. Adsorbent-Soil Samples

The soil samples collected showed a slight variation in clay content Cambodian agronomic soil classification system (CASC) with 10% and 6 %. Organic matter (OM) content varied from 0.5 % to 0.3% for Kwale red soil and sediment respectively. Table 4.1 below gives a summary of the adsorbent properties. Adsorption to soils and sediments is probably the most influential factor on the transport and fate of organic contaminants in the environment. The extent of the sorption to soil and sediment affects not only the contaminant level in an ecosystem, but also the movement and fate of the contaminant as well [Chiou and Kile, 2000].

Table 4.1. Properties of adsorbents used.

Profile	Red soil	Ngong river sediment
Soil depth cm	Top	Top
Soil pH-H2O (1:2.5)	5.5	7.2
Elect. Cond. mS/cm	0.52	0.18
* Carbon %	5	3
Sand %	78	80
Silt %	12	14
Clay %	10	6
Texture Class	Sl	Ls
Cat. Exch. Cap. me%	5.2	6.8
Calcium me%	3.1	8.9
Magnesium me%	0.9	3.1
Potassium me%	0.8	0.6
Sodium me%	1.1	0.8

Sum me%	5.8	13.4
Base %	100+	100+
ESP	21.5	12.1

Table 4.1 above show the varous properties that were obtained in the red soil and the sediment characterization. It was observed that there was slight variation in content between the two samples. From the nature of the environments where these samples were collected, it is noted that the sediment is less acidic compared to the red soil. The red soil has a higher organic carbon (5%) than sediment (3%). The difference in the organic carbon levels has a significant change in terms of the adsorption rate.

4.2.2. Kinetic Study

In this study, adsorption kinetics showed an immediate adsorption and attained a pseudo adsorption equilibrium within period of three hours for both the red soil and the sediment. After pseudo equilibrium, there was minimal difference of captafol concentration in the adsorbate even after 24 hours observed as shown in Figure 4.20. Beck and Jones [1996] found in their study of the sorption of atrazine and isoproturon that the herbicides were adsorbed from the solution in the first hour of the 24 h sorption experiments. A rapid initial adsorption of captafol is a surface phenomenon. The hydrophobic nature of captafol resulted to the rapid filling of the empty adsorption sites during the initial steps, which followed a linear variation. This was followed by a slow migration and diffusion of the compound. This led to a drastic decrease in adsorption rate as shown in figure (4.2.1), into the organic matter matrix and mineral structure [Gao *et al*., 1998]. Parkpian *et al*. [1998] observed this trend in the study of endosulfan on Rangsit lowland soils and Phrabat upland soils [Mathava and Ligy, 2005].

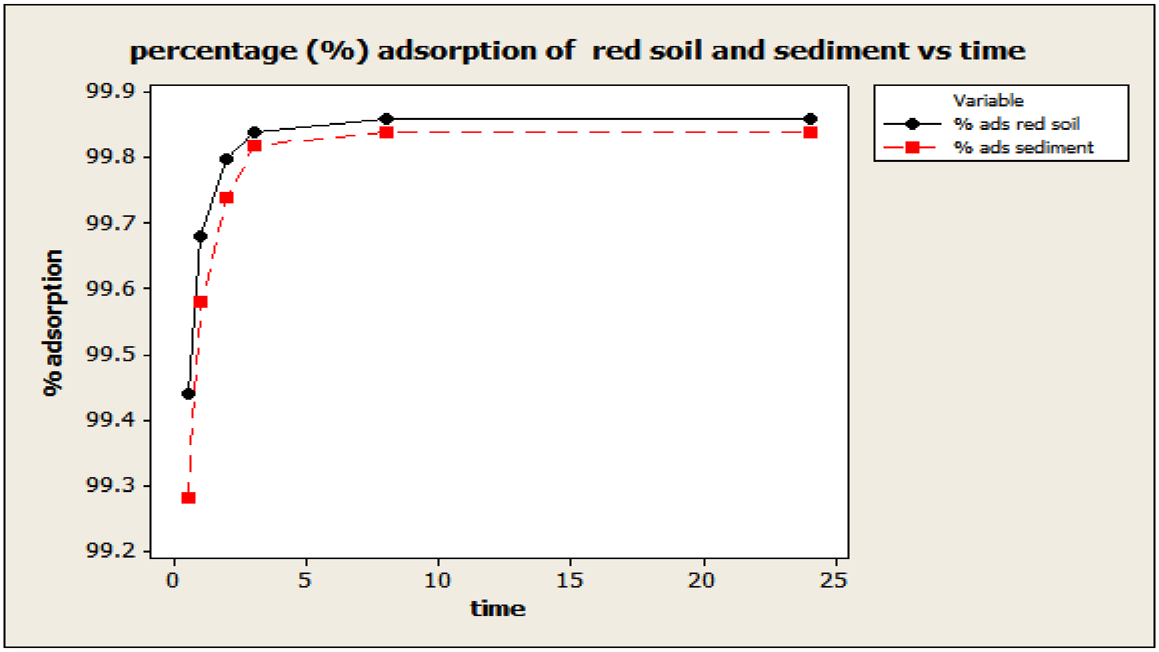

Figure 4.2.1. Percentage adsorption of captafol on red soil and sediment as a function of time

It is evident from the results that the adsorption of captafol is fast during the initial stages and the portion of pesticide taking part in the long term behavior is insignificant as compared to that participating in the preliminary phase of rapid adsorption. The kinetic rate was estimated using Lagergren pseudo first order model [1898] and Ho`s pseudo second order model [1995]. The first order is given by;

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

While the second order equation is;

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

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

The adsorption rate was found to follow pseudo second order rate with the sediment adsorbing at 0.0245 mg/min and red soil at 0.035 mg/min. The observed rates due to the fact that the red soils contain more organic carbon content than the sediment hence the higher adsorption rate.

The following table shows data for pseudo second order rate for captafol adsorption.

Table 4.2: Data for second order rate of captafol adsorption

Time (h)	Qe (mg/g) for red soil	Qe (mg/g) for sediment
0	0	0
0.5	0.5	0.5
1	0.85	0.7
1.5	1.2	1
2	1.4	1.2
2.5	1.5	1.3
3	1.6	1.4

The following figure shows the plot of the pseudo second order rate of adsorption.

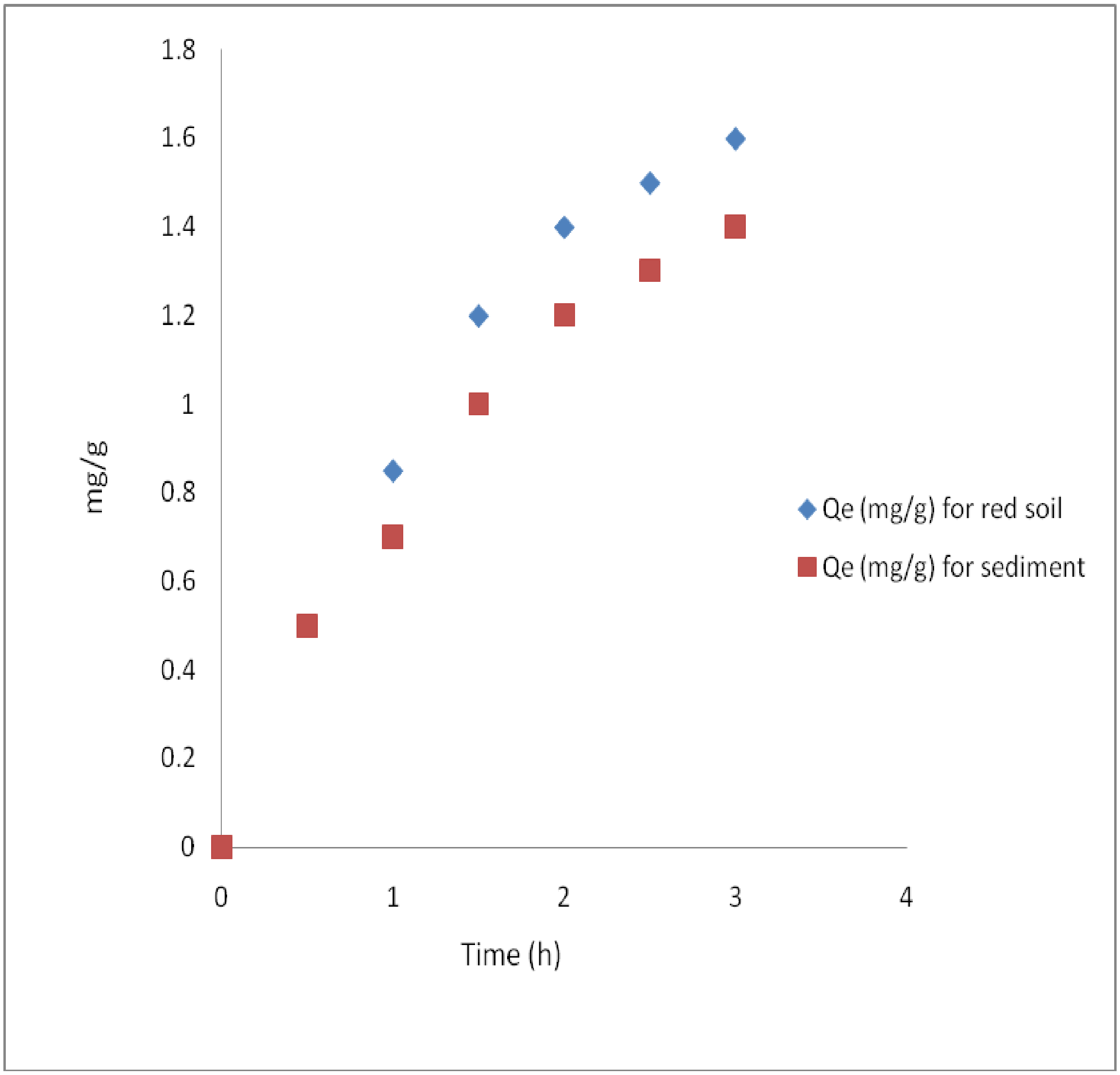

Figure 4.3:The rate of adsorption of captafol on red soil and sediment.

4.2.3. Equilibrium Study

The behavior of captafol adsorbed was studied at room temperaure with equilibration time of 3 hours. The freundlich and Langmuir isotherms were used. Both the freundlich and Langmuir coefficients were calculated as shown in Table 4.2 below. The values of the variables calculated show how they vary with increasing equilibration time.

Table 4.3: Calculated freundlich variables for sediment.

Sediment	Equilibration tim (min)	N	K’	G	r^2
	30	1.04	49.56	-9.67	0.956
	60	1.09	58.18	-10.07	0.969
	120	1.1	60.39	-10.16	0.971
	180	1.1	61.22	-10.03	0.971
	Average	1.08±0.03	57.34±4.6	-9.98±0.19	

Calculated values of Freundlich constants for red soil are shown in Table 4.3. The number of adsorption sites (n) and the Gibbs free energy (G) were the same at all equilibration times. The apparent equilibrium constant (K’) showed a slight deviation. The above results show consistency and precision of the results obtained. A favorable adsorption tends to give Freundlich variable *n* a value between 1 and 10. Larger value of n implies strong interaction between adsorbent and pesticide. When *n* equals to 1 indicates linear adsorption leading to identical adsorption energies for all the sites. From the equation

$\ln[X]_{ads}=\ln (nK')+n \ln([X]e +[SXn]w)$, the value of *n* is the slope of the graph whle the *y* intercept the value for *ln* (nK'). The value for ΔG is obtained from the equation -ΔG = RT In K'.

The above trend was also observed in the red soil as shown below.

Table 4.4: Calculated freundlich variabless for red soil.

Red soil	Equilibration time (min)	N	K'	G	r^2
	30	1.08	50.2	-9.7	0.978
	60	1.11	60.13	-10.15	0.969
	120	1.104	62.25	-10.24	0.974
	180	1.11	60.06	-10.12	0.961
	Average	1.10±0.01	58.16±4.7	-10.05±0.21	

Calculated langmuir constants are shown in Table 4.5 below. The data shows that adsorption was higher in red soil than the sediment. This is due to the fact that red soil contains more carbon content than the sediment. It also show that just like in the freundlich adsorption model, the amount of captafol adsorbed onto the adsorbate increased with longer equilibration time. This is illustrated in table 4.5 below.

Table 4.5: Calculated langmuir coefficients.

Sediment	Equilibration time (min	Qmax	B	r^2
	30	0.0329	156.96	0.823
	60	0.023	112.86	0.872
	120	0.0039	625	0.933
	180	0.0053	479.39	0.919
Red soil	Equilibration time (min	Qmax	B	r^2
	30	0.0155	227.27	0.893
	60	0.0033	714.29	0.868
	120	0.0025	897.67	0.952
	180	0.0034	699.79	0.908

The following figures shows the relationship between q_e versus c_e for langmuir isotherm as well as $ln[X]_{ads}$ versus $ln\ ([X]_e + [SX_n]_w)$ for freundlich isotherm:

A. Freundlih isotherms

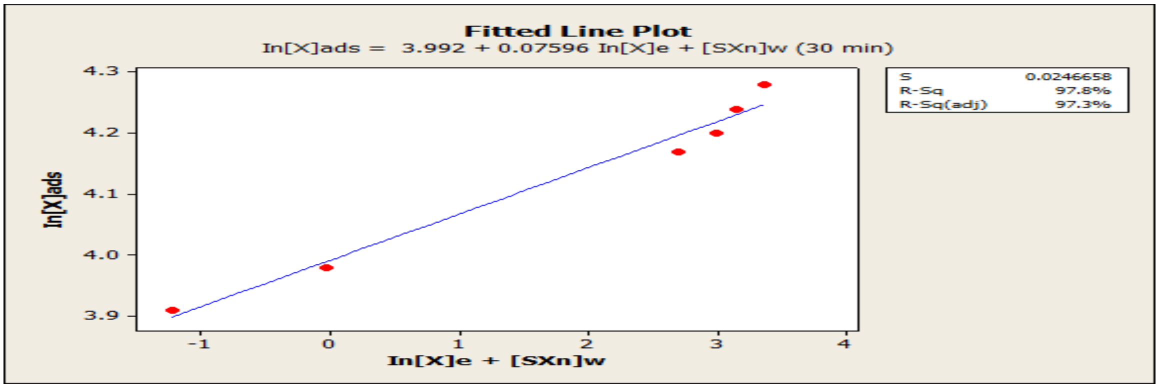

Figure 4.4. Freundlich isotherm for red soil (shaking time of 30 minutes).

Freundlich isotherm for red soil showed good correlation with a coefficient of 0.976.

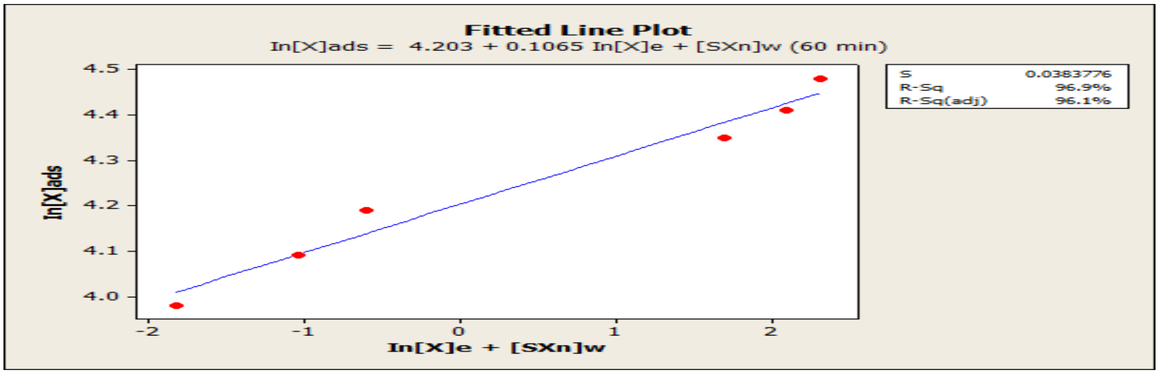

Figure 4.5. Freundlich isotherm for red soil (shaking time of 60 minutes).

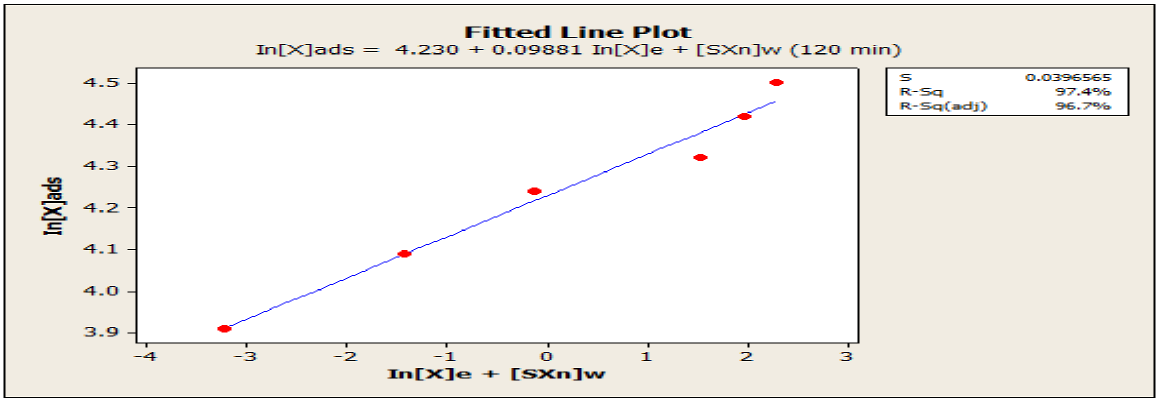

Figure 4.6. Freundlich isotherm for red soil (shaking time of 120 minutes).

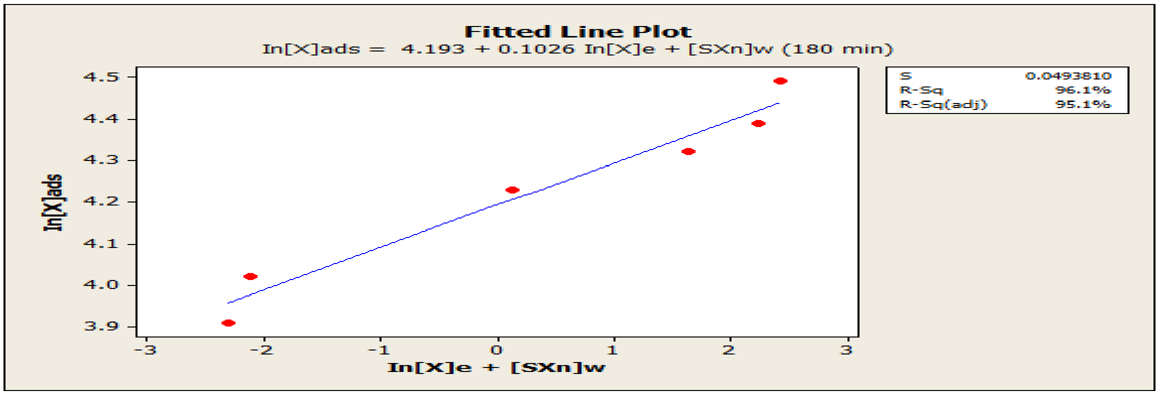

Figure 4.7. Freundlich isotherm for red soil (shaking time of 180 minutes).

The adsorption isotherms (Figures 4.7 to 4.18) fitted to both the Freundlich and Langmuir isotherm equations. The typical graphical representations of the linearised plots are shown in the figures below for adsorption of captafol on both the sediment and the red soil, respectively.

The results show that the adsorption process could be described well with both Freundlich and Langmuir isotherms. The experimental equilibrium data fitted well with correlation coefficient values greater than 0.9 for freundlich as reported in a related work [Tella and Owalude, 2007; Kehinde *et al.*, 2008]. The freundlich model was also found to give a better fit in the adsorption of captafol.

Similarly, plots for the sediment were made as shown in the following figures.

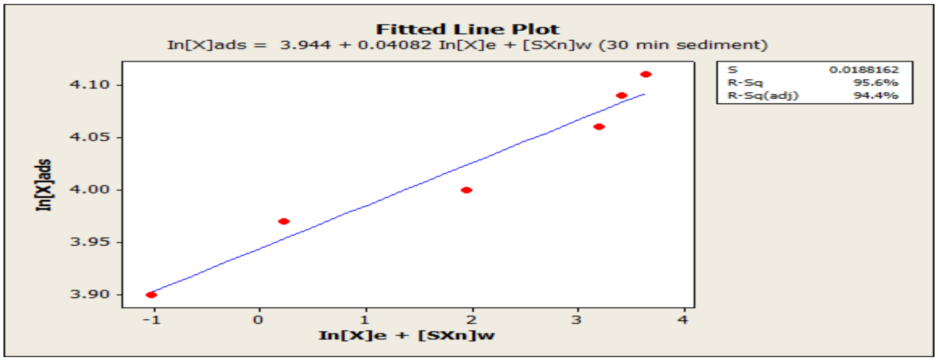

Figure 4.8: Freundlich isotherm for sediment (shaking time of 30 minutes).

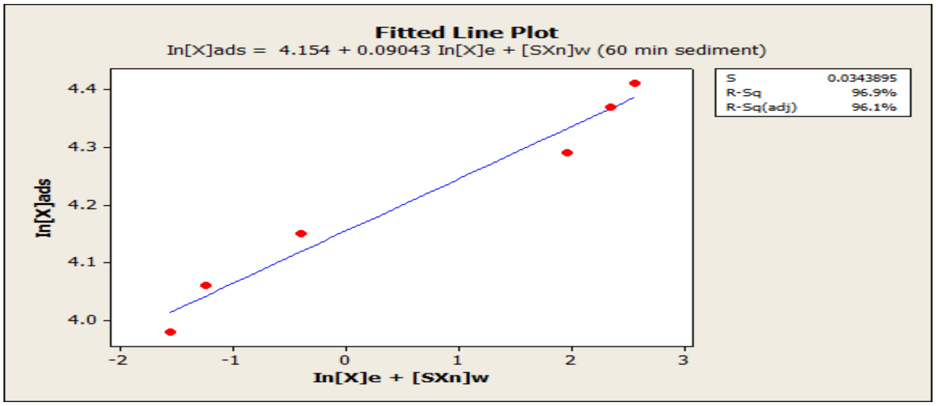

Figure 4.9: Freundlich isotherm for sediment (shaking time of 60 minutes).

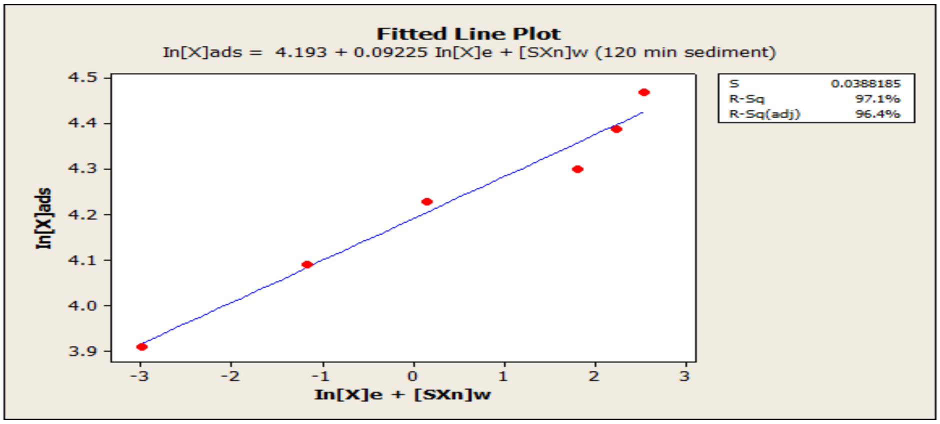

Figure 4.10: Freundlich isotherm for sediment (shaking time of 120 minutes).

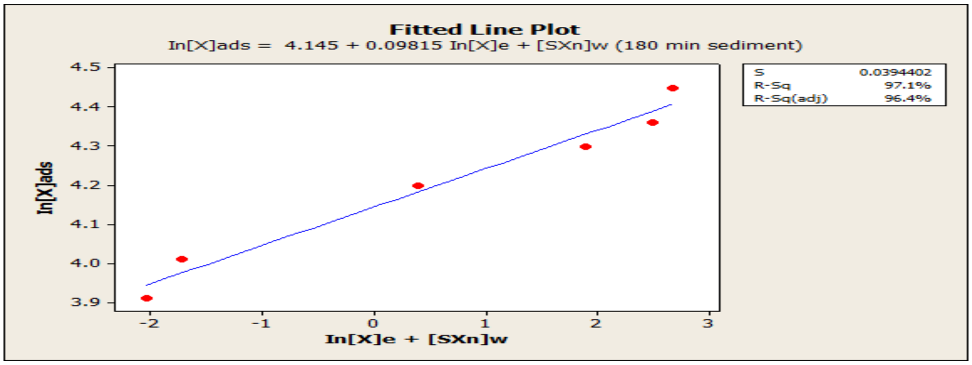

Figure 4.11: Freundlich isotherm for sediment (shaking time of 180 minutes).

The above figures show the effect of increasing equilibration time.

B. Langmuir isotherms

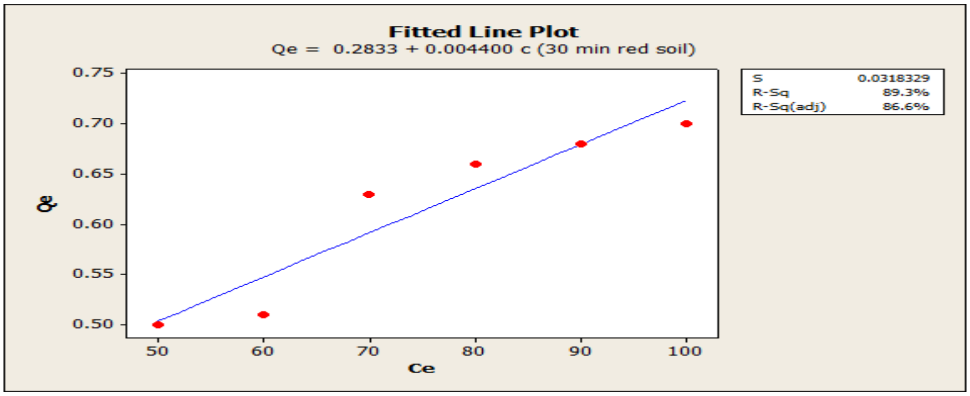

Figure 4.12. Langmuir isotherm for red soil (shaking time of 30 minutes).

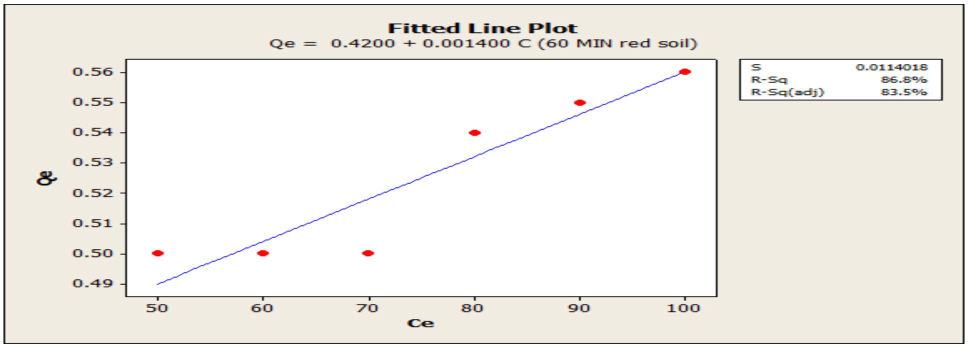

Figure 4.13: Langmuir isotherm for red soil (shaking time of 60 minutes).

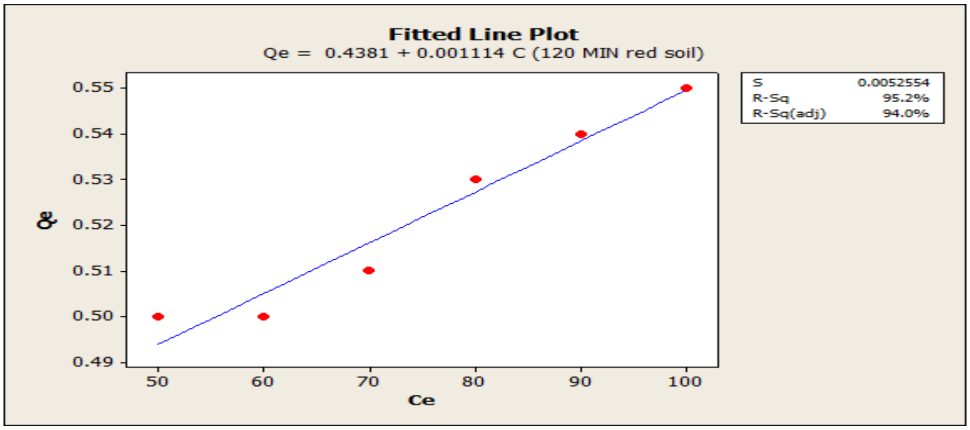

Figure 4.14: Langmuir isotherm for red soil (shaking time of 120 minutes).

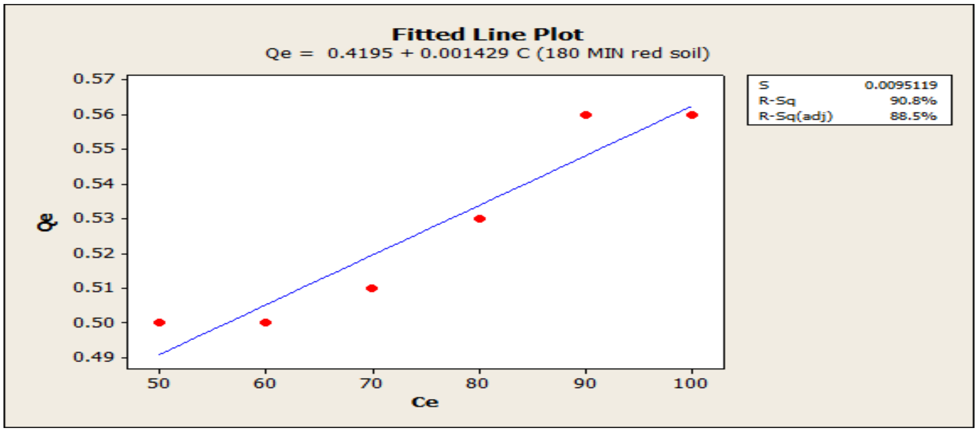

Figure 4.15: Langmuir isotherm for red soil (shaking time of 180 minutes).

The same Langmuir plots were also made for the sediment for various shaking times. The figures below show their behavior.

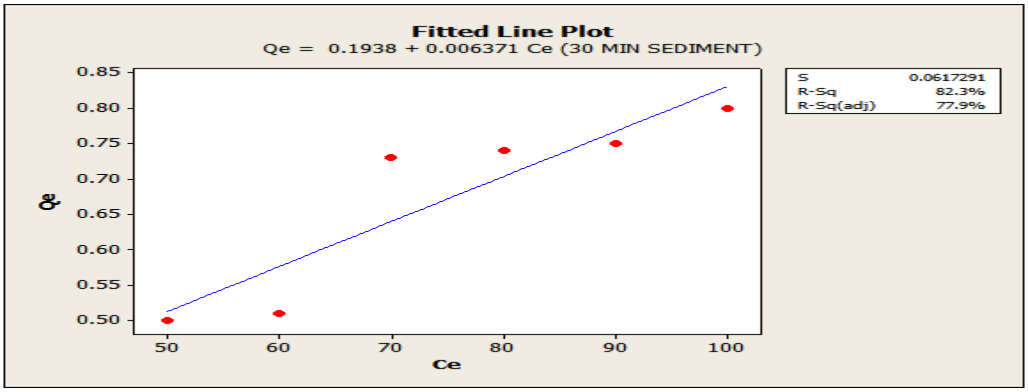

Figure 4.17: Langmuir isotherm for sediment (shaking time of 30 minutes).

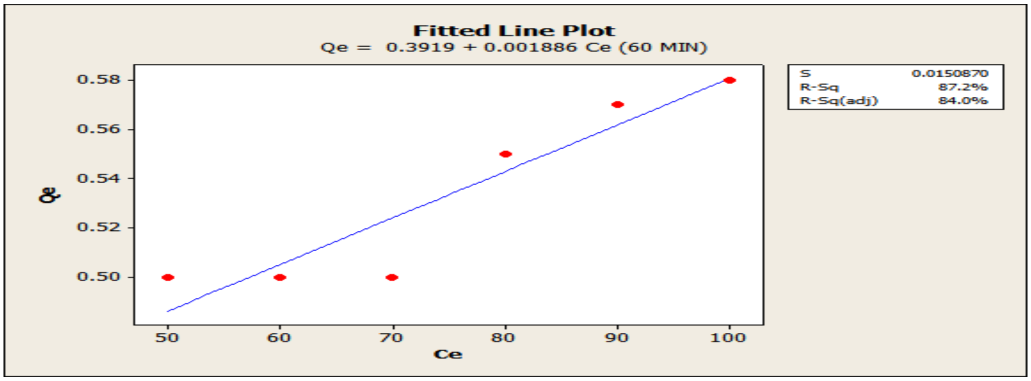

Figure 4.17: Langmuir isotherm for sediment (shaking time of 60 minutes)

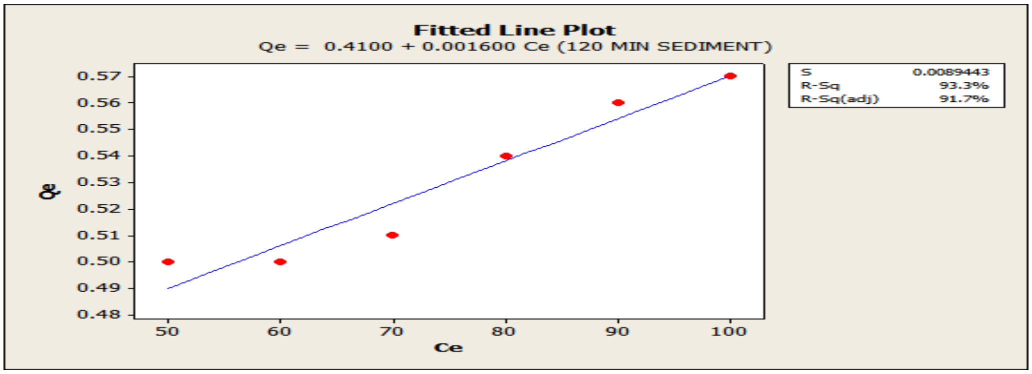

Figure 4.18: Langmuir isotherm for sediment (shaking time of 120 minutes)

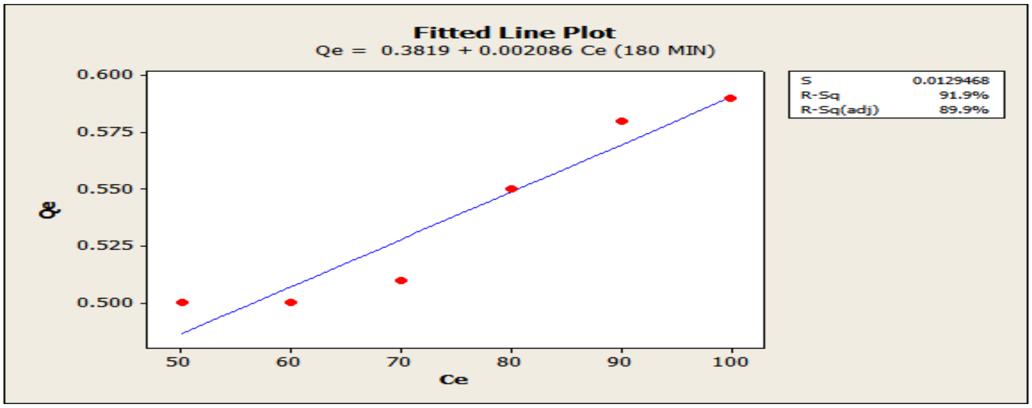

Figure 4.19: Langmuir isotherm for sediment (shaking time of 180 minutes)

It is evident from the data that the adsorption of captafol followed freundlich isotherm better than Langmuir. Soil is heterogeneous material hence adsorption followed the freundlich isotherm unlike the Langmuir which represents a monolayer and homogeneous or uniform adsorption

The trend above 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 freundlich adsorption constant for red soil was 58.15 and 57.34 for the sediment. Red soil has more vacant sites or surface area compared to the sediment particles. This observation is in line with what was reported earlier by Gao *et al*. [1998], where they found out that 2,4-D adsorbed more in soils than the sediment. The organic matter in red soil was (5%), which increased the captafol adsorption. On the other hand, sediment has fewer pores and adsorption sites (organic matter is 3%), which resulted in minimum captafol adsorption. The results of Freundlich and Langmuir isotherms are indicated in Tables 4.5and 4.6, respectively.

Table 4.5 below shows the data used in plotting the freundlich isotherm for red soil. Natural logarithm of the aqueous concentration (ln [X]e+ $[SX_n]$ w) and the adsorbed concentration ($\ln[X]_{ads}$) was determined.

Table 4.6 Data for freundlich isotherm (red soil).

shaking tim	initial concentration(ppm)	([X]e [SXn]w)	ln[X]ads	ln ($[X]_e$ $[SX_n]_w$)	$\ln[X]_{ads}$
30	50	0.28	49.72	-1.23	3.91
	60	0.97	59.03	-0.03	3.98
	70	14.76	55.24	2.69	4.17
	80	19.8	60.2	2.99	4.2
	90	23.4	66.6	3.15	4.24
	100	28.9	71.1	3.36	4.28

60	50	0.16	49.84	-1.83	3.98
	60	0.13	59.87	-1.04	4.09
	70	0.52	69.48	-0.61	4.19
	80	5.5	74.5	1.7	4.35
	90	8.14	81.86	2.1	4.41
	100	10.1	89.9	2.31	4.48
120	50	0.04	49.96	-3.22	3.91
	60	0.24	59.76	-1.43	4.09
	70	0.88	69.12	-0.13	4.24
	80	4.6	75.4	1.53	4.32
	90	7.16	82.84	1.97	4.42
	100	9.76	90.24	2.28	4.5
180	50	0.1	49.9	-2.3	3.91
	60	0.12	59.88	-2.12	4.09
	70	1.14	68.86	0.13	4.23
	80	5.1	74.9	1.63	4.32
	90	9.3	80.7	2.23	4.39
	100	11.2	88.8	2.42	4.49

From the initial concentrations, the absorbance of captafol in solution ([X]e + [SXn]w) was obtaine`d using UV-Vis NIR spectrophotometer. The Beer's law was used to calculate its concentration. The Beer's law is given by:

A=εcl where,

A is the absorbance, ε is the molar absortivity which was equivalent to 0.006709 L $mol^{-1}cm^{-1}$, *c* is sample concentration and *l* is the path length which was 1 centimetre.

The adsorbed concentration, ($[X]_{ads}$) was obtained by subtracting the concentration in the solution ([X]e+ [SXn]w) at equilibrium. For example, for equilibration time of 30 minutes and initial concentration of 50 ppm. To obtain $[X]_{ads}$, 50- 0.28=49.72. Then the natural logarithm of the concentration in the solution (ln $\{[X]_e + [SX_n]_w\}$) and adsorbed concentration ($\ln[X]_{ads}$) was calculated. The natural log of 0.28 is -1.23 and that of 49.72 is 3.91. The same was done to the other set of data.

Table 4.7 below shows the data used in plotting the freundlich isotherm for sediment. Natural logarithm of the aqueous concentration (ln [X]e + [SXn]w) and the adsorbed concentration ($\ln[X]_{ads}$) was determined.

Table 4.7: Data for freundlich isotherm (sediment).

shaking time	initial concentration(ppm)	([X]e - [SXn]w)	[X]ads	ln ($[X]_e$ - $[SX_n]_w$)	ln[X]ads
30	50	0.36	49.64	-1.02	3.9
	60	1.26	58.74	0.23	3.97
	70	19.19	50.81	1.95	4
	80	25.75	54.25	3.2	4.06
	90	30.32	59.68	3.41	4.09
	100	37.6	62.4	3.63	4.11
60	50	0.21	49.79	-1.56	3.98
	60	0.18	59.82	-1.24	4.06
	70	0.68	69.32	-0.39	4.15
	80	7.2	72.8	1.97	4.29
	90	10.6	79.4	2.36	4.37
	100	13.13	86.87	2.57	4.41
120	50	0.05	49.95	-3	3.91
	60	0.31	59.69	-1.17	4.09
	70	1.15	68.85	0.14	4.23
	80	6	74	1.8	4.3
	90	9.31	80.69	2.23	4.39
	100	12.69	87.31	2.54	4.47
180	50	0.13	49.87	-2.04	3.91
	60	0.16	59.84	-1.73	4.01
	70	1.49	68.51	0.4	4.2
	80	6.63	73.37	1.89	4.3
	90	12.09	77.91	2.49	4.36
	100	14.56	85.44	2.68	4.45

Similarly, the above calculation was done for the Langmuir isotherm for sediment and the red soil. The data obtained is presented in tables 4.8 and 4.9 below.

Table 4.8: Data for Langmuir isotherm for sediment.

shaking time	initial concentration(ppm)	Aqueous conc	Adsorbed conc	Q_e	C_e
30	50	0.36	49.64	0.5	50
	60	1.26	58.74	0.51	60
	70	19.19	50.81	0.73	70
	80	25.75	54.25	0.74	80
	90	30.32	59.68	0.75	90
	100	37.6	62.4	0.8	100
60	50	0.21	49.79	0.5	50
	60	0.18	59.82	0.5	60
	70	0.68	69.32	0.5	70
	80	7.2	72.8	0.55	80
	90	10.6	79.4	0.57	90
	100	13.13	86.87	0.58	100
120	50	0.05	49.95	0.5	50
	60	0.31	59.69	0.5	60
	70	1.15	68.85	0.51	70
	80	6	74	0.54	80
	90	9.31	80.69	0.56	90
	100	12.69	87.31	0.57	100
180	50	0.13	49.87	0.5	50
	60	0.16	59.84	0.5	60
	70	1.49	68.51	0.51	70
	80	6.63	73.37	0.55	80
	90	12.09	77.91	0.58	90
	100	14.56	85.44	0.59	100

Table 4.9: Data for Langmuir isotherm for red soil.

shaking time	initial concentration (ppm)	Aqueous conc	Adsorbed conc	Q_e	C_e
30	50	0.28	49.72	0.5	50
	60	0.97	59.03	0.51	60
	70	14.76	55.24	0.63	70
	80	19.8	60.2	0.66	80
	90	23.4	66.6	0.68	90
	100	28.9	71.1	0.7	100
60	50	0.16	49.84	0.5	50
	60	0.13	59.87	0.5	60
	70	0.52	69.48	0.5	70
	80	5.5	74.5	0.54	80
	90	8.14	81.86	0.55	90
	100	10.1	89.9	0.56	100
120	50	0.04	49.96	0.5	50
	60	0.24	59.76	0.5	60
	70	0.88	69.12	0.51	70
	80	4.6	75.4	0.53	80
	90	7.16	82.84	0.54	90
	100	9.76	90.24	0.55	100
180	50	0.1	49.9	0.5	50
	60	0.12	59.88	0.5	60
	70	1.14	68.86	0.51	70
	80	5.1	74.9	0.53	80
	90	9.3	80.7	0.56	90
	100	11.2	88.8	0.56	100

4. 3 Effect Of Concentration Of Captafol On Adsorption

Equilibrium study was carried out for different concentrations of captafol. It was clear that the at higher initial concentration of the captafol solution, there was a rapid decrease in concentration then it was followed by slow decrease as equilibrium time approached. At lower initial concentration, the decrease in concentration was lower than at higher concentrations. This was due to vacant surfaced of the adsobent that was being filled up by the pesticide. The following Figure 4.19 illustrates the observed changes.

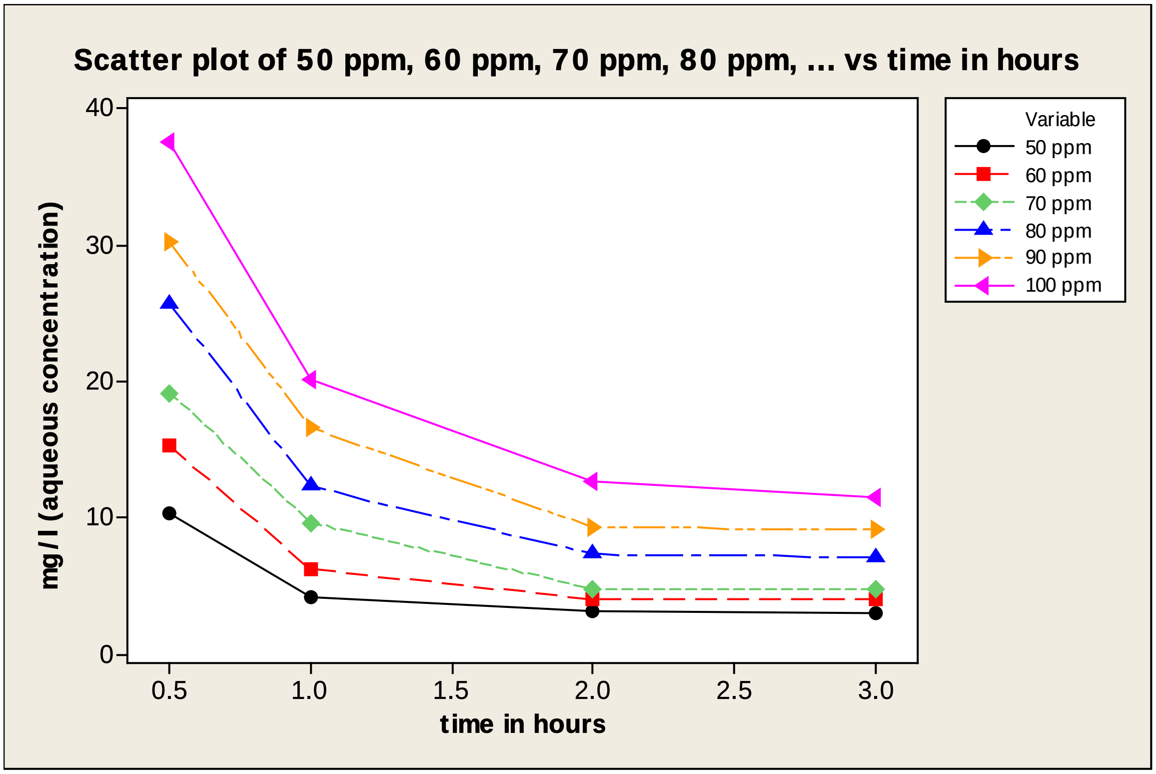

Figure 4.20: Effect of concentration on adsorption.

Equilibrium was attained within 3 hours. Hence this shaking time was found to be appropriate for optimum adsorption and was used in all subsequent experiments. The experimental results of adsorption of captafol on both the sediment and red soil at various initial concentrations of 50, 60, 70, 80, 90 and 100 mg/l with contact time are shown in

Figure 4.20. The data revealed that the percent adsorption increases with the increase in initial pesticide concentration as the actual amount of pesticide adsorbed per unit mass of adsorbent increased with increases in captafol concentration. This implies that the adsorption is highly dependent on the initial concentration of the pesticide.This is because at lower concentration the ratio of the initial number of captafol molecules to the available surface area is low. However, at higher concentration the available sites of adsorption becomes fewer , and hence the decrease in the rate of adsorption.

4.4 Effect of Shaking Time

Shaking time plays a vital role in the adsorption process. It is obvious that the amount of adsorption increases with shaking time increasing. The maximum adsorption capacity was observed after 3 hours, beyond which there was almost no further increase in adsorption (Figure 4.21).

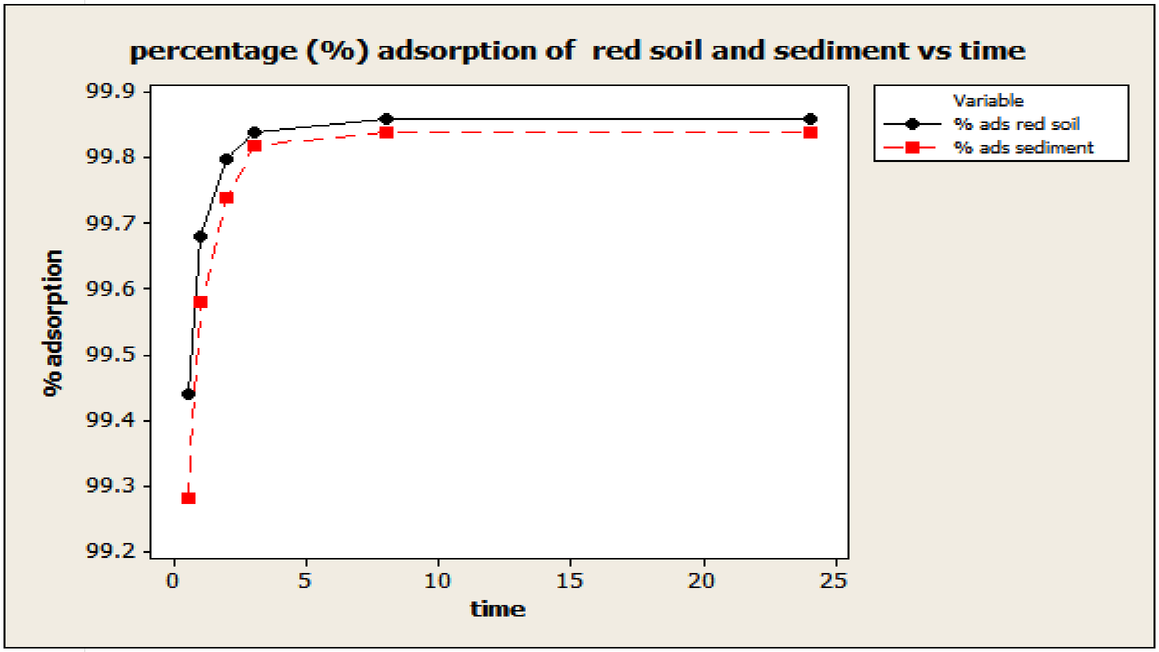

Figure 4.21. Percentage adsorption of captafol on red soil and sediment as a function of time.

From Figure 4.21 it is seen that the adsorption of captafol exhibits saturation kinetic as the quantity of bound captafol stagnates after approximately 3 hours minutes for both the sediment and red soil, meaning that the chances of further adsorption is very small. The higher adsorption rate at the initial stages may be due to an increased number of vacant adsorption sites on the adsorbent available at the initial stage [Kumar and Vadivelan 2005; Uddin *et al*., 2007]. The reduction in the adsorption of captafol with time could be due to the accumulation of captafol particles in the vacant sites leading to a decrease in adsorption percent at time 3-24 hours. The reduction in the percentage of captafol adsorbed as a result of increased contact time was not significant, since most of the pesticide was already absorbed.

4.5 Effect Of Organic Matter Content (OM) On Captafol Adsorption

Properties of sediment and red soil were nearly similar, except for the pH. The red soil's pH is a bit lower than that of the sediment. Organic matter content in the soils plays crucial roles in the determination of the extent to which adsorption/desorption takes place. Organic matter in the soil does not only modify adsorption or leaching of pesticides, in some cases it reduces pollution of groundwater by pesticides (Abdelhafid *et al*., 2000). Moreover, this can accelerate or increase biodegradation by the stimulation of microorganisms due to nutrient incorporation (Cox *et al*., 2001 and Sdinchez *et al*., 2004).

From the results above (table 4.1), both the sediment and the red soil contained some organic matter (OM). Most of soil OM consists of humic compounds that have not been exhaustively characterized but have a very high cation exchange capacity. The humic compounds have functional groups such as carboxyl, amino and phenolic hydroxyl, which provide sites for hydrogen bonding with pesticide molecules. Together, these characteristics provide a very considerable capacity for pesticide adsorption and increased persistence. The OM content in the red soil which was slightly higher than the sediment probably influenced the migration of captafol to it (Berglof *et al*., 2002, Yu and Zhou, 2005). The affinity between pesticide and soil particles is dependent on soil and pesticide properties. A high proportion of pesticide molecules are adsorbed by soils high in OM content and/or high clay content (Huggenberger, Farmer and Letey 1973). The calculated rate of desorption of captafol was found to be 0.035 mg/min and 0.0245 mg/min for the red soil and sediment, respectively. It was noted that the OM content in the red soil was 5%, which probably influenced the migration of captafol molecules to it (Berglofet al., 2002; Yu and Zhou, 2005). According to Martins and Mermoud (1998), an increase in the organic contents increased sorption of the nitroaromatic herbicide Dinoseb by either specific charge related mechanisms or non-specific partitioning. These results are in line with Iraqi (2000), when he demonstrated that, beyond 2% organic matter in soils, adsorption of parathion took place almost entirely on the organic surfaces. In comparison to the red soil, the reduction in OM content in sediment resulted to reduction in adsorption of the insecticide. This suggests that little amounts of organic amendment may greatly influence captafol adsorption, more so when added to soils relatively poor in organic matter. Another important factor to note is that the extent to which minerals contribute to adsorption depends on the ratio of clay minerals to soil organic carbon contents [Spark and Swift, 2002]. Soil with high OM may retain the pesticide and reduce the chances of contaminating the surface as well as groundwater sources. Decline in OM content caused an 18% decrease in adsorption rate captafol. This may be due to the difference in interaction of captafol with the organic molecules.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Adsorption of captafol in the red soil and the sediment followed Freundlich isotherm better than the Langmuir isotherm. Organic matter content of soil has significant influence on the adsorption of captafol. Soil with high organic matter content has better pesticide's adsorption ability. Red soil has higher organic matter content and exhibited enhanced captafol adsorption capacity than the sediment. The increase in initial concentration also led to increased adsorption capacity.

The results of this study showed that the adsorption process was exothemic and sponteneous. This was evident from the the Gibbs free energy (ΔG) value of -9.98±0.19 kj/mol and -10.05±0.21kj/mol for sediment and red soil, respectively. The negative values of Gibb's free energy (ΔG) indicated that the feasibility of the adsorption process and spontaneous adsorption of captafol. The exponent n is the number of pesticide molecules associated with a single adsorption site, S, to give the pesticide-site complex SX_n.The value of n obtained for sediment and red soil was 1.08±0.03 and 1.10±0.01, respectively. This suggests that each molecule of captafol is associated with single adsorption site. This is only conceivable if we regard the adsorption site as being a single colloidal particle. The major adsorption interactions which bind small organic particles in the soil environment involve soil particles of colloidal dimensions, that is, 1nm to 1mm [Burchill *et al.*, 1981]. The apparent equilibrium constants for the sediment and red soil were 57.34±4.6 and 58.16±4.7, respectively.

The results from the present study would help in designing of effective fungicide management strategies. This also highlights the feasibility of adverse effect of soil adsorbed captafol on the succession crops.

5.2 Recommendations

From the results obtained in this study, the following reommendations were made:

1. To reduce pesticides contamination in the soil and possible bioaccumulation through food, pesticides of great danger to human should be identified and used carefully or banned.

2. Reduce pesticides usage on bare and slopy areas where pesticides can reach drinking water by run off.

3. Soil content of organic matter should be increased by using manure and compost. This will increase the soil biological activity and its ability for adsorption as well.

4. Farmers should be taught on how to use various pesticides and their impact on the environment.

5. Further studies should be done on the extent to which level the adsorbed pesticides get to the crops that are applied.

6. Further studiesto be done on other parameters that influence retention of pesticides that were not investigated. Such parameters could require other types of instrument that are currently not available in the department of chemistry.

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