KINETIC STUDIES OF MALATHION DISSIPATION/ DEGRADATION IN LAKE VICTORIA WATER IN THE PRESENCE OF ZEOLITE

BY

OGUNAH, ATIENO JOANNE

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DEPARTMENT OF CHEMISTRY

MASENO UNIVERSITY

ABSTRACT

Malathion is an organophosphorus pesticide widely employed in controlling pests in agriculture, household, stored grains, greenhouse, forestry and public health. Malathion usually adsorbs on soils and through surface runoff or leaching, it finds its way into rivers and lakes whose waters the local population rely on for their domestic use. The current water treatment methods are not efficient in getting rid of malathion and its degradation products. Zeolites which are crystalline aluminosilicates with tetrahedral framework structure enclosing cavities can be effective alternatives for mopping malathion from water due to their abilities to abstract and enhance degradation of water pollutants. Although zeolites have been reported to degrade malathion faster, the kinetics of such zeolitic action has not been documented. The objective of this study was to determine the degradation kinetics of malathion in fresh water and to compare the effectiveness of Faujasite X and Y in removal of malathion. Experiments were set up in a laboratory at 27°C and repeated three times. Water samples were collected from Asembo bay (0°10'S, 34°25'E) and different concentrations (10 and 20 ppm) of malathion spiked in the water samples. After 1, 2, 4, 6 hours and thereafter increasing the previous time upto 768 hours, 40 mL was sampled from each concentration, extracted using dichloromethane and cleaned on a florisil column then analyzed using GC-NPD to determine the concentrations and GC-MS for confirmation of the degradation products. Quantification was based on peak area responses using the internal standard method and concentrations corrected for recovery. The solid Faujasites were characterized using IR to establish if there was adsorption in the zeolite matrix and XRD to determine any changes in the position of the Na^+. The data was linearly regressed to obtain the relationship between time and malathion concentration. Malathion degradation in fresh water followed a pseudo first order kinetics with a rate constant of -0.144 ± 0.010 hr^{-1}. The calculated

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Being a country whose economy highly depends on agricultural activities, Kenya advocates for the use of pesticides in agriculture to enhance production. This is beneficial as it raises productivity and reduces post harvest losses (Gonzalez, 1988). The use of pesticides inevitably leaves behind residues on the crops, on stored grains, in the atmosphere and in the soil, which may be bioavailable to the consumers including animals (Suett, 1980). These pesticide residues, may finally find their way into rivers and lakes whose waters the local population depend on for their domestic use, through surface run off and leaching. Though, the pesticides are degraded by various environmental factors in the aquatic environment, their degradation products still remain in the waters (Suett, 1980).

Lake Victoria is situated at $0^{o}21'N$ - $3^{o}0'S$, $31^{o}39'$ - $34^{o}53'$ E astride the equator on an altitude of 1240 m above the sea level with a surface area of 68,800 square kilometers (Ogutu-Ohwayo *et al.*, 2002). Catchment areas surrounding the lake are agricultural zones where sugarcane, rice, maize and tea among other crops are grown (Ogutu-Ohwayo *et al.*, 2002). Fertilizers and pesticides used on these farms may eventually end in the lake. The lake plays a vital role in supporting the millions of people living around its shores, in one of the most densely populated regions of the earth (Ogutu-Ohwayo *et al.*, 2002). Furthermore, the lake is a major water reservoir and a source of water for domestic, industrial and commercial purposes to a total population of nearly 5 million in several major towns and urban centres within the basin as well as several rural villages which get their water supply untreated from the lake and the rivers within the basin. The primary purpose of any water treatment is to remove the pollutants from the water and make the water fit for human consumption and domestic use. The pollutants can be partially removed by biological treatment whose aim is to lower the pathogenic count

of micro organisms in the water (Banerji, 1999). Biodegradation of pollutants is very effective in degrading pesticides especially under laboratory conditions; however under field conditions the results are equivocal. Current water treatment methods are not efficient in getting rid of most pesticides and their degradation products (Anil, 1987; Banerji, 1991; MSUE, 2003) which could equally be poisonous (Mehlhorn and Armstrong, 2001).

Osewe (2010) reported that the presence of zeolites in water enhances the decomposition of pesticides. Zeolites, due to their nature may not only degrade the pesticide faster, but also trap the pesticide molecules in their cages by binding them thereby significantly reducing the pesticide molecules level in water (Yang *et al.*, 2006). Zeolites degrade malathion faster (Patterson *et al.*, 2006), however, the extent and exact kinetics of such zeolitic action have not been studied. Both X and Y types of zeolites can adsorb and chemically decompose both organo-phosphates such as dimethyl methylphosphonates (Yang *et al.*, 2006) and organochlorides (Kanyi *et al.*, 2006). Systematic adsorption tests have shown that organo-zeolites help remove atrazines, lindane and diazinon from waters (Jonan *et al.*, 2006). However, application and comparison studies between zeolite-X (low Si/Al ratio) and zeolite-Y (high Si/Al ratio) together with the determination of the rates and order of malathion degradation reactions in the presence of zeolites need to be done.

This study investigated the exact degradation kinetics of malathion in Lake Victoria water in the presence of zeolites and generated information on comparative studies of degradation reactions of malathion in Lake Victoria water with zeolites X and Y.

1.2 Statement of the Problem

Delivery of clean water to consumers for drinking and domestic requirement is still a major challenge in Kenya and more so in eliminating pesticide residues in this water. This study was carried out to evaluate the potential of utilizing zeolites to manage the concentration of malathion and its degradation

products in fresh water sourced from Lake Victoria and hence make valuable recommendation to the concerned authority.

1.3 Hypothesis

1.3.1 Null Hypothesis

Zeolites can not be used to enhance the chemical degradation and abstraction of malathion and its degradation products from fresh water.

1.3.2 Alternative Hypothesis

Zeolites can be used to significantly aid in chemical degradation and abstraction of malathion and its degradation products in fresh water.

1.4 Broad Objective

To determine the degradation kinetics of malathion in fresh water and compare the effectiveness of Faujasite X and Y in the removal of malathion.

1.5 Specific Objectives

1. To determine the half-life of malathion and its degradation rate in fresh water
2. To establish the degradation products of malathion in water with and without the zeolites
3. To infer the mechanism of malathion degradation in the presence of zeolites X and Y respectively
4. To compare the effect of zeolite X and Y on the degradation rate of malathion in fresh water

1.6 Justification of the Study

The use of organophosphate pesticides including malathion in Kenya is increasing with increase in agricultural production. In developing countries, the illnesses due to pesticides are more common than in developed countries depending on the amount of pesticides used (Vorley and Keeney, 1998). Pesticides contaminate water systems through spray drift or run offs from agricultural fields (USEPA, 2002, 2003), and find their way into the human system when consumed and also through consuming animal products contaminated with pesticide residues. Toxicological effects of pesticides on human include birth defects in children, incontinence and convulsions and fatality amongst others (NRC, 1977). There is therefore, the need to reduce the quantities of pesticide residues eventually consumed by human beings. Lake Victoria serves as a water source for the local community who use it untreated for their domestic use and for their animals too. This makes the community susceptible to malathion contamination. Zeolite is viewed as a safe, cheap, readily available and re-usable method of treating water for both domestic and commercial use by absorbing and degrading pesticide residues (Patterson *et al.*, 2006).However the degradation rate and the mechanism of degradation of malathion in the presence of zeolite X and Y in fresh water is not known and this current study was aimed at availing this information.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Pesticide Use

Pesticides are chemical substances (or mixtures of substances) intended for the purpose of preventing, destroying, repelling, or mitigating any pests or for use as a plant regulator, defoliant or desiccant (McKenna and Cuneo, 1993). Pesticides generally include insecticides, herbicides, fungicides and rodenticides. The use of pesticides in agriculture is a worldwide practice that is considered beneficial since it raises production and reduces post harvest losses (Gonzalez, 1988). Pesticides are also used in the protection of human health and welfare. In the tropics, apart from their use in boosting food and agricultural productivity, pesticides play a vital role in controlling insect vectors of endemic diseases (Anon, 1976). The use of these pesticides has adverse effects on the environment and animal health. The United States Environmental Protection Agency (USEPA) had estimated that, world wide, there occurs between 10,000 and 20,000 diagnosed pesticide illnesses and injuries among agricultural workers per year (USEPA, 2003). In developing countries, the mortality and illness due to pesticides are relatively more common than in developed countries in relation to the amount of pesticides used (Vorley and Keeney, 1998).

Lack of awareness on the handling and application techniques of pesticides by the farmers in the developing countries is the major cause of exposure, as compared to the developed countries where most of the pesticides originate from. The other challenge that faces the use of pesticides in the developing countries has been the rising cost of pesticides, insect pest resurgence, pest resistance and pesticide nonspecificity. Organochlorine pesticides are more lipophilic and are considered to be more persistent and bioaccumulative at various trophic levels in the food web (Morifuse, 1976). For instance,

1,1- (2,2,2-dichloroethylidene) *bis* (4-chlorobenzene) (DDT), whose use was much publicized by the World Health Organization (WHO) for the eradication of malaria was banned due to its persistence and bioaccumulation in the fatty tissues of the human body and its negative impact on reproduction in birds and fish (McEwen and Stephenson, 1979). This led to the replacement of most organochlorine pesticides with organophosphorus, such as malathion which are generally short lived and less biomagnifiable (Pimentel, 1973).

The organophosphorus (OP) compounds first appeared in the market in 1945 as a result of the successes of the German industry in finding modifications of the chemical warfare agents, useful for insect control. The first to appear were tetraethylpyrophosphate (TEPP) and *O, O*-diethyl *O*-4-nitrophenylphosphorothioate (parathion), followed by S-1, 2-*bis* (ethoxycarbonyl) ethyl *O, O*-dimethylphosphorodithioate (malathion) and many others, four years later (Bey-Dyke *et al.*, 1970; Brown, 1978).

2.2 Malathion

Malathion, S-1, 2-bis (ethoxycarbonyl) ethyl *O, O*-dimethylphosphorodithioate (Worthing, 1979) was discovered in 1950 as a low mammalian toxicity organophosphorus insecticide and was introduced in the same year by the American Cyanamid Company under the code number EL4B049 and protected by USP 2578652. Malathion is synthesized by addition of methanol to phosphorus pentasulphide, forming dimethyl phosphorodithioic acid. This is then added directly to maleic acid diethyl ester under reflux with the influence of catalytic quantities of alkali (Rouy and Gros, 1983).

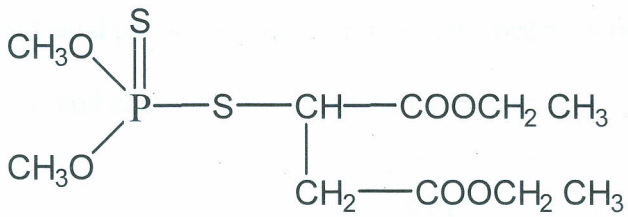
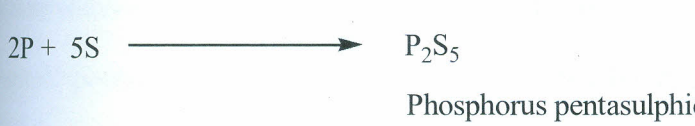
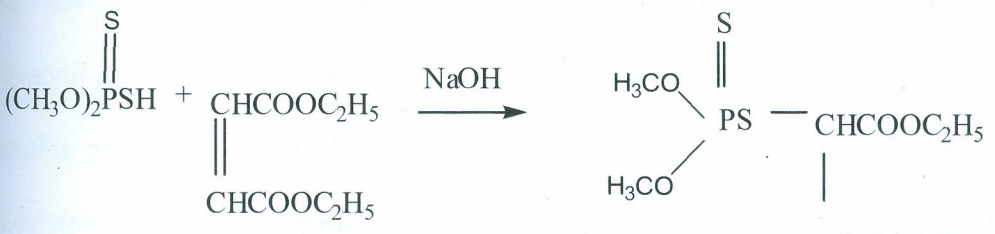


Figure 1: Chemical structure of S-1, 2-bis (ethoxycarbonyl) ethyl *O, O*-dimethylphosphorodithioate (malathion) (www.pesticides.gov.uk)



Phosphorus pentasulphide

Dimethyl phosphorodithioic acid



Maleic acid diethyl ether

Malathion

Scheme 1: Synthesis of Malathion (Schmidt and Fest, 1973).

The chemical and physical properties of malathion have been documented as summarized in Table 1.

Table 1: The physical and chemical properties of malathion.

Boiling point	156-157°C
Melting point	2.9°C
Molecular weight	330.36
Log $K_{o/w}$	2.36
Water solubility	143ppm at 20°C(deionized water)
Vapour pressure	7.9×10^{-6}mmHg at 20°C
Density	1.23 g/ml
Henry's law constant	2×10^{-8} atm m^{-3}/mol
Acute oral LD_{50} for rats	2800 mg/kg

$K_{o/w}$ – Octanol-water partition coefficient
Source: Howard (1991)

The high margin of safety of malathion as compared to other pesticides to mammals and its selectivity against target insects, coupled with its amenability at ultra low volume applications make it a good general purpose contact insecticide employed in controlling insects of household, home, garden, stored grains, greenhouse, agriculture, forestry and public health (Mulla *et al.*, 1981).

Malathion has low mammalian toxicity in spite of its strong insecticidal properties. Although it has little or no cholinesterase activity, like many other organophosphates, malathion is activated by mono-oxygenase attack to produce the potent anticholinesterase inhibitor malaoxon. Malathion and malaoxon are rapidly detoxified in mammals by carboxylesterase attack (but not in insects) to produce their respective monacids referred to as malathion monocarboxylic acid and malaoxon monocarboxylic acid.

If the carboxylesterase detoxification pathway is inhibited, mammals may be made almost as susceptible to malathion as insects (Caldwell, 1983).

Effects of malathion on human are similar to those observed for other organophosphates, except that larger doses of malathion are required to produce them. Single dose of 30 mg/day malathion may affect the immune system response of man (Gallo and Lawryk, 1991). Symptoms of acute exposure to the organophosphate may include numbness, incoordination, headache, tremor, nausea, abdominal cramps, blurred vision, and difficulty in breathing or respiratory depression (ATSDR, 2001).

One of the major problems related to hazardous nature of malathion is the presence of impurities in the formulated material. These impurities may arise either as by products or they may form as degradation products (see Table 2) during storage of the technical product (Ware, 1992). Pure malathion is not very toxic but crude malathion and its formulations contain impurities which are toxic to mammals (Anon, 1997).

Table 2. Toxicity of malathion and its degradation products through oral route in rats.

Compound	Oral LD_{50} (mg/kg)
Malathion	1375
Malaoxon	215
DMPT	694
DMDTP	4510
MCA	5615
DCA	5544

Source: Mehlhorn and Armstrong (2001)

Malathion comes in a variety of formulations depending on factors such as nature of the target species, the desired persistence and the method of application. It is formulated as dust, wettable powders, emulsifiable concentrate and as aerosols, it has low thermal and alkaline stability (Ware, 1992).

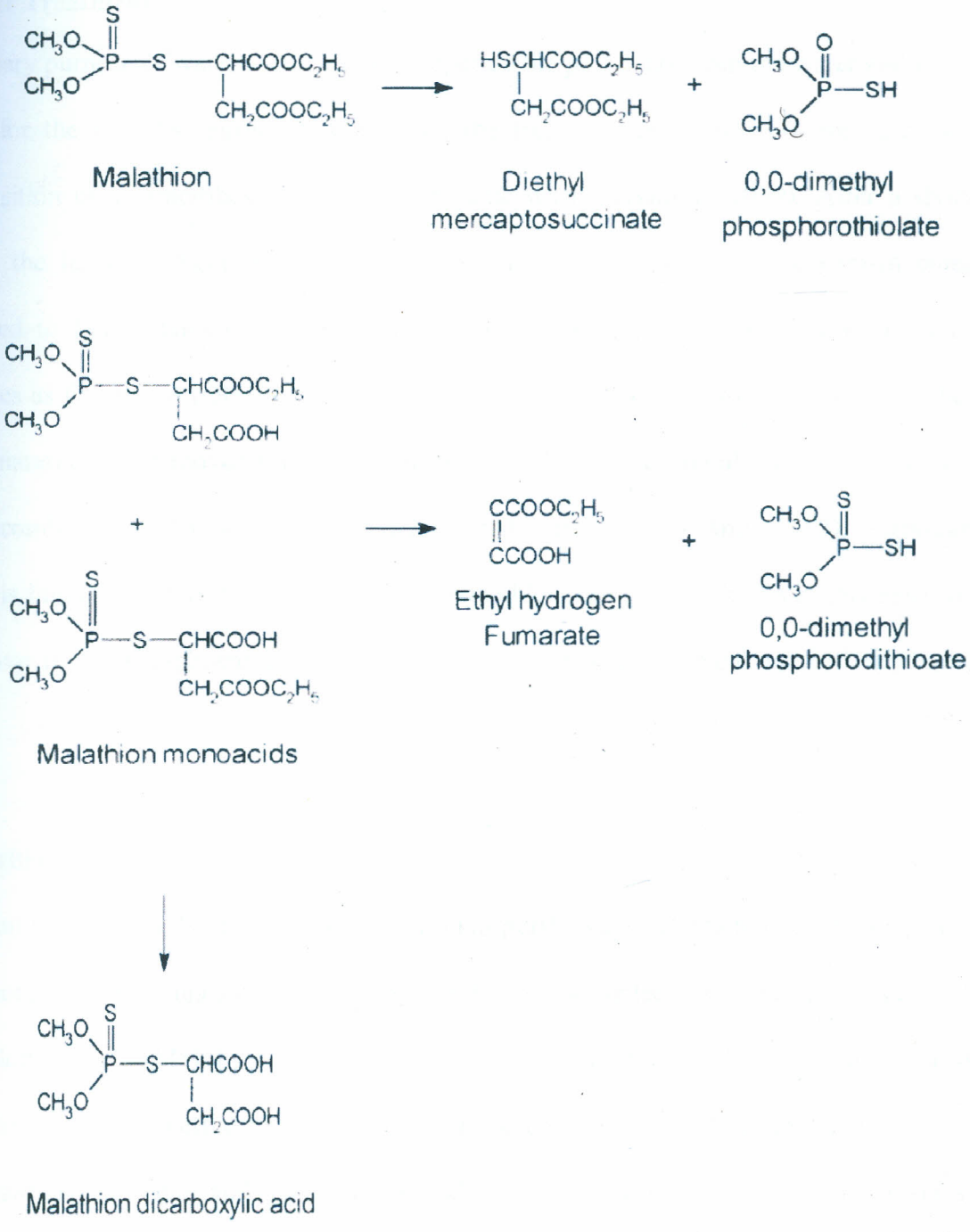
2.2.1 Malathion Degradation in Water

Degradation of malathion in water is pH dependent as it degrades quickly in water with pH >7.0 (Newhart, 2006). Hydrolysis is the main route of degradation in alkaline aerobic conditions. The half-life of malathion in water ranges from 0.2 weeks at pH 8.0 to 21 weeks at pH 6.0. Metabolites resulting from hydrolysis include malaoxon, malathion alpha and beta monoacid, diethyl fumarate, diethyl thiomalate, *O*, *O*-dimethylphosphorodithioic acid, diethylthiomalate, and *O*, *O*-dimethylphosphorothionic acid (see Scheme 2). Biodegradation also plays a role when pH <7.0 and the rate of hydrolysis is slow relative to the rate of biodegradation. Breakdown constituents of biodegradation include beta monocarboxylic acid, dicarboxylic acid, and diethyl thiomalate (Neal *et al.*, 1993).

Malathion is also readily oxidized in water to malaoxon by a variety of mild oxidizing reagents. Thus, it is generally recognized that malathion is easily oxidized to malaoxon by swimming pool chlorine concentrations (Scharf, 2003). For instance, malaoxon has greatest persistence when pool water is acidic, and malathion is stable in oxygen saturated water at a pH 5 for up to two weeks (ATSDR, 2005). Sunlight shortens both malathion and malaoxon half-lives in pools to 3 days. These data suggest that little accumulation of malathion or malaoxon in swimming pools occurs, but does indicate that they can persist at low levels for a considerable period of time (Howard, 1991).

In river water, the half-life of malathion is generally less than one week. For example, in the Suwanee River USA, with large amounts of tannins, malathion was 50% degraded by sunlight within 16 hours. However, malathion may remain stable in distilled water for three weeks and its photolysis half-life is 41 days. Applied at up to 2.7 kg per acre in logged ponds for mosquito control, it is generally effective for 2.5-6.0 weeks. In seawater, degradation increases with salinity. Breakdown products in acidic water are mono- and dicarboxylic acids such as dimethyl phosphorothionic acid and 2-mercaptodiethyl

succinate (Wolfe *et al.*, 1975). The degradation mechanisms of malathion in water therefore depend on the type and composition of the solvent water. No mechanism and degradation products of malathion in the presence of zeolite have been reported.



Scheme 2: Degradation pathway of malathion through hydrolysis (Wolfe *et al.*, 1976).

2.3 Water Treatment

The primary purpose of water treatment is to separate the pollutants from the water and make the water suitable for the intended purposes. Generally, the treatment procedure involves aerobic biological decomposition using microbes to get rid of organic wastes (Banerji, 1999). After a short treatment duration, the liquid effluent with much lower organic matter and micro organism composition is chlorinated to kill pathogenic microorganisms, and thereafter treated with lime to eliminate ionic phosphates as $Ca_5 (PO_4)_3(OH)$ at a high pH when NH_4^+ is converted to gaseous NH_3. The remaining organic materials are removed through adsorption on activated charcoal and finally nitrogen removed through combined action of nitrifying and denitrifying bacteria (Anil, 1987). Although activated charcoal is highly effective in the removal of toxic chlorinated organics, it's highly selective and does not remove the organophosphates (Anil, 1987). Other water treatment method that could be used include;

2.3.1 Distillation

Distillation is a process that relies on evaporation to purify water. Contaminated water is heated to form steam. Inorganic compounds and large non-volatile organic molecules do not evaporate with the water and are left behind (MSUE, 2003). The steam then cools and condenses to form purified water. Distillation is most effective in removing inorganic compounds such as metals (iron and lead) and nitrate; hardness (calcium and magnesium); and particulates from a contaminated water supply. The boiling process also kills microorganisms such as bacteria and some viruses (MSUE, 2003). The effectiveness of distillation in removing organic compounds varies, depending on such chemical characteristics of the organic compound as solubility and boiling point. Organic compounds that boil at temperatures greater than the boiling point of water (some pesticides) can be effectively removed from the water (MSUE, 2003). Organic compounds that boil at temperatures lower than the boiling point of

water (benzene and toluene) will be vaporized along with the water. If these harmful compounds are not removed prior to condensation, they will recontaminate the purified product (MSUE, 2003). This method is the most expensive since it requires electricity.

2.3.2 Reverse osmosis

Reverse osmosis (RO) is a membrane technical filtration method that removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on one side of a selective membrane (Barneji, 1999). The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be "selective," this membrane should not allow large molecules or ions through the pores (holes), but should allow smaller components of the solution (such as the solvent) to pass freely. Edwards and Schubert (1974) reviewed some of the early separation results of herbicides and pesticides with RO membranes. They also conducted studies with the herbicide 2,4-D and found separations were <51%. It was noted that solute adsorption could occur on the cellulose acetate membranes. This method is very effective against most inorganics but requires activated carbon to reduce organics (Anil, 1987).

2.4 Zeolites

2.4.1. History of Zeolite

In recent years there have been considerable research efforts in the field of zeolite chemistry and synthesis. There are 34 known natural zeolites and about 190 zeolites without natural counterparts, thus synthesized. Of this large number, only a few have found commercial application (Breck, 1974). A zeolite is defined as a crystalline aluminosilicate with a tetrahedral framework structure enclosing cavities occupied by cations and water molecules, both of which have enough freedom of movement, thus permitting cation exchange and reversible dehydration. The term zeolite was used originally to

describe just such a material. Later, however, the term broadened to include all ion exchangers, natural occurring and synthetic inorganic materials as well as organic ones (Smith, 1993). The empirical formula of zeolite is

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot wH_2O$$

Where M represents the exchangeable cation of valence n, w is the number of water molecules per unit cell, x and y are the total number of tetrahedral molecules per unit cell (Gonghu, 2005).

2.4.2 Composition and structure of zeolite

The fundamental building block of all the zeolites is a tetrahedron of four oxygen anions surrounding a small silicon or aluminum ion. The tetrahedral (T-units) are then arranged so that the zeolite has an open framework structure, which defines a pore structure with a high surface area (Bhatia, 1990) (Figure 2). This surface area is different from that of amorphous solids such as silica-alumina in that it is a 3D part of the crystalline solid.

Zeolites have the following properties; open cage like structures, high cation exchange capacities, high internal and external surface areas, variable aggregate sizes and high permeability (Satterfield, 1980). These properties are dependent on the topology of the zeolite framework, the size, shape and accessibility of its free channels, the location of charge and the size of the cations within the framework, the presence of faults and occluded material, the ordering of T-atoms (T= Si or Al) and their local environment (Rabo, 1976).

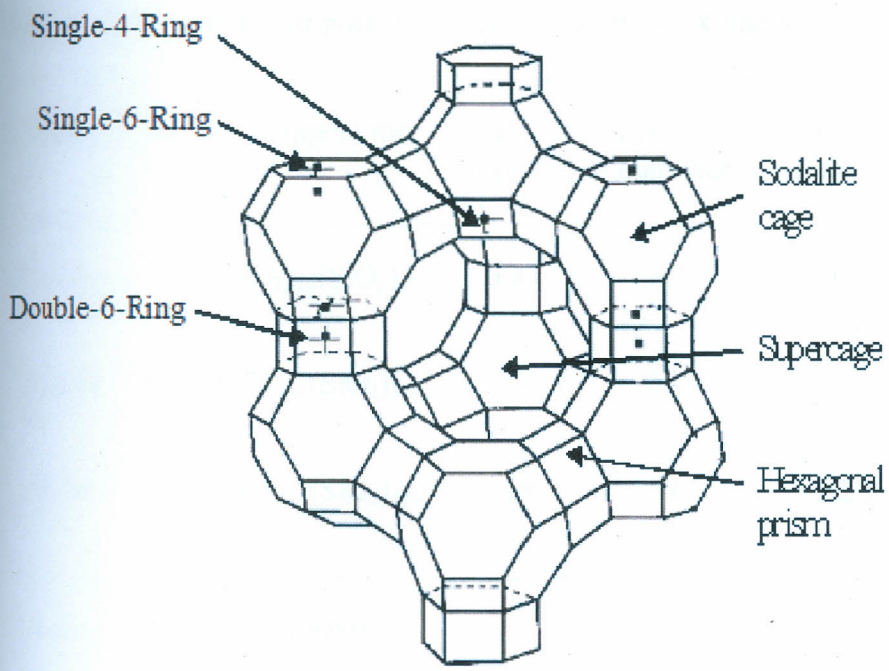


Figure 2: Structure of faujasite zeolite X and Y (Maxwell, 1982)

Faujasite zeolite X and Y consist of tetrahedra linked together to form the so-called sodalite cage units which are approximately 0.26 nm in size. The sodalite interconnection creates a three dimensional structure with a twelve ring window of approximately 0.74 nm in diameter for a "supercage" of approximately 1.18 nm diameter (Kowenje *et al.*, 2006). They are synthesized by reacting SiO_2 and Al_2O_3 as sources of cations with NaOH (Bhatia, 1990). Although zeolite X and Y have the same structure they differ in their composition and chemical behaviour, as shown in Table 3 below.

Table 3. Composition and pore diameters of zeolite A, X and Y

Type	unit cell composition	Void volume ml/ml	Pore diameter Å	Si/Al ratio	Thermal decomposition temperature °C
Zeolite A	$Na_{12}(AlO_2)_{12}(SiO_2)_{12}$	0.47	4.2	1	700
Zeolite X	$Na_{86}(AlO_2)_{86}(SiO_2)_{106}$	0.50	7.4	1-2.5	772
Zeolite Y	$Na_{56}(AlO_2)_{56}(SiO_2)_{136}$	0.48	7.4	>2.5	793

Source: Satterfield, (1980)

2.4.3 Zeolite catalysis

Zeolite catalysis has found application in many areas of the oil refining and petrochemical industries and it is continuing to grow in importance (Maxwell, 1987). Most catalytic studies with zeolite have used the synthetic X and Y zeolites. This is due to the fact that their minimum pore opening in the three- dimensional porous structure is about 8Å which will allow passage of all but the largest hydrocarbons. Therefore, while the effects of diffusion are surely significant during catalysis, they should be less with the X and Y zeolites than with the smaller pore zeolite such as zeolites A (Bhatia, 1990). Generally zeolites have four properties that make them especially useful for heterogeneous catalysis. They have exchangeable cations allowing the introduction of cations with various catalytic properties, their pore diameters are less then 10Å and their pores have one or more discrete sizes (Gates and Schuit, 1979; Satterfield, 1980).

Zeolites X and Y have been reported to adsorb and chemically decompose dimethyl methylphosphonate (DMMP), used extensively as a nerve agent stimulant (Yang *et al.*, 2006) and it is an organophosphate. In Belgrade the presence of zeolite in waste water was reported to have enhanced

the decomposition of malathion (Patterson *et al.*, 2006). However, the exact kinetics of such zeolitic action is not yet documented.

2.5 Suitability of zeolite for water treatment

Zeolite X and Y have large pores into which molecules can be adsorbed, and after dehydration the exchangeable cations can be modified by chemical treatment therefore permitting control of chemical forces on the sorted molecules, which favour them to be used as catalysts (Eberly, 1976). Since they are abundant in nature, due to the high percentage of aluminum and silicon on the earth crust (Arnold, 1996), this makes zeolites cheap and easily available for use and besides they can be regenerated (Eberly, 1976).

2.6. Characterization of zeolites

2.6.1 X-ray diffraction (XRD) analysis of faujasite zeolites

The purpose of XRD is to determine the unit cell parameters. When the zeolitic structure is known, then one can infer if an element has been introduced into the lattice framework position (Verdine, 1992). Zeolites X and Y particularly for catalyst and adsorbent applications are major articles of manufacture and commerce. As such X-ray is therefore used to monitor these zeolites providing a number more or less closely related to percent zeolites in the sample (ATSM, 2008). Drastic changes in intensity of individual peaks in the XRD patterns of zeolites Y and X may result from changes in the distribution of electron density within the cationic sites of the zeolites. The electron density distribution is dependent upon molecules. Intensity changes may also result if some or all of the cations in Y and X are exchanged by other cations (ATSM, 2008). Diffraction line [311] at 11.6^{o} 9 (2θ) and [300] at 9.9^{o} (2θ) are the characteristic lines which indicate the migration of site I (double six ring) and site II (single six ring) Na^{+} ions (Bouvy *et al.*, 2006).

Kowenje *et al.*, (2010) employed the use of XRD to study the effect of ammonia in Cu (II) exchanged X zeolites. Similarly Kokotailo and Fyfe (1995) analyzed the zeolites structure using the powder X-ray diffraction and established that perturbations in the framework structure, crystal morphology, extra framework material, phase purity, crystallite size, and the setting and occupation of cation sites can produce differences in the x-ray patterns.

2.6.2 Infrared analysis of faujasite zeolites.

This spectroscopic method is applied in the chemical characterization of zeolites samples. Somerset *et al.* (2004) employed the use of infrared technique for chemical characterization of faujasite zeolites and reported that strong bands 3480-3500 cm^{-1} can be attributed to the presence of hydroxyls in the faujasite supercage and also in the sodalite cages. The faujasite supercage consists of the sodalite cages and is its building blocks and therefore its presence will be shown in the IR spectrum.

Similarly, Karge (1980) reported that pore opening vibrations seem to be related to a complex motion which in total includes an opening rupture of the rings (4-rings, 6-rings) of the structure. In the far IR region (200-50cm^{-1}), vibrations of the cations against the framework occur. The IR bands of alkali metal-exchanged zeolites X and Y shift to lower frequencies (red shift) with increase in cation mass (Karge, 1980). Kovo and Edoga (2005) used the IR technique to prove that the Ahako clay has the same properties as the zeolites by comparing the IR peaks of the clay with those of the zeolites.

2.7 Analytical method for malathion

Malathion being a polar compound can be extracted from water using dichloromethane as a solvent. Since malathion is converted to the monocarboxylic acids, the acids can then be analysed using IR, while GC-ECD can further be used to quantitatively measure the amount of malathion present (Zheng

and Hwang, 2006). Also solid phase extraction (SPE) and elution of malathion from water has been done with n-hexane and diethyl ether in a ratio 1:1 and the concentrated samples analysed by the GC-MS with ion trap detection (Keith *et al.*, 1999).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals

The solvents: n-hexane, dichloromethane and diethyl ether used were supplied by Kobian Kenya Ltd and were all AR grade .Analytical grade anhydrous Na_2SO_4, and NaCl (both 99% pure), Florisil PR grade, activated charcoal PR grade and Whatman No. 1 filter papers were also obtained from Kobian Kenya Ltd. Malathion analytical standard and zeolite NaX and NaY were purchased from Sigma-Aldrich Inc (St. Louis, USA).

3.1.2 Instruments

Instruments used included; Vulcan oven (model A-550, Dentsply International, USA), analytical balance (Sartorius BP 210S, Germany), suction pump (model 7049-05, Chicago, USA), rotary evaporator (Eyela N-100, Japan), gas Chromatograph (Varian chrompack, Japan), FT-IR spectrometer (Equinox 55, Japan) and X-ray diffractometer (Scintag XDS 2000, Germany).

3.2 Activation of zeolite

One hundred grams of zeolite samples (X and Y), in a round bottomed flask were activated by connecting the flask to a suction pump and pumping for 30 minutes, after which the zeolite was heated using a Vulcan A-550 oven at 70°C for 30 minutes. The temperature was then increased to 100°C and heating done for a further 30 minutes. This was repeated at 130°C for 30 minutes and finally at 150°C for 4 hours still under vacuum of ca. 10^{-2} torr. The zeolites were then considered activated (Kowenje *et al.*, 2006) and were used for the experiments.

3.3 Sample Collection and Treatment

Forty litres of Lake Victoria water, was collected from Asembo Bay ($0^{o}10'S$, $34^{o}25'E$), 100 m into the lake from the shore by immersion on the surface waters. The initial pH of the water was measured; after which the water was filtered into a black plastic container using Whatman No. 1 filter paper to remove the suspended particles.

3.4 Experimental Design

The research was set up at Maseno University chemistry laboratory, with three set-ups of three replicates each at $27^{o}C$ as described below.

3.4.1 Set up 1

One litre (1 L) water sample was measured and transferred into a 2 L glass jar. Two grams (2 g) activated zeolite X was measured using a Sartorius BP 210S analytical balance and dispersed in the water in the jar.

3.4.2 Set up 2

Separately, one litre water sample was measured and transferred into a 2 L glass jar. Into the jar, 0.01 g of malathion earlier dissoved in 3mls of acetone was added to make 10 ppm of malathion .Another one litre water sample was measured into a separate 2 L glass jar to which 0.02 g of malathion in 3mls of acetone was added to make 20 ppm of malathion. Stirring was done to ensure dissolution of malathion into the water.

3.4.3 Set up 3

In another set up, one litre water sample was measured and transferred into a 2 L glass jar to which 0.01 g of malathion in 3ml of acetone was added. Two grams of zeolite X was weighed and added to the jar then stirred. Another one litre water sample was measured into another 2 L jar, 0.02 g of malathion in 3 ml of acetone and 2 g of zeolite X were added to the second jar.

3.5 Sampling for analysis of water samples

After 1 hr from the time of treatment, 40 ml each was transferred to clean labeled amber bottles from each of the jars in the three set ups and the pH measured. Another 40 ml was again drawn from the solutions and the pH measured after 2, 4, 6, 12, 24, 48, 96, 192, 384 and 768 hours. Set ups 3.3.1, 3.3.2 and 3.3.3 were also repeated for zeolite Y.

3.6 Extraction of analytes

Solvent extraction was done following the method of Zweig and Devine (1969) where 40 ml sample was transferred the into a 100 ml separating funnel. Two grams sodium chloride was added to the sample to salt out the pesticide from the aqueous phase. A 20 ml volume of triple distilled dichloromethane was then added to the mixture and shaken for 5 minutes, with periodic venting to release pressure (Zweig and Devine, 1969). The mixture was allowed to stand for 10 minutes until aqueous and organic layers clearly separated out. The aqueous layer was drained into a second separatory funnel and the organic layer transferred into a clean 100 ml Erlenmeyer flask containing 2 g anhydrous sodium sulphate to dry the extract. Another 20 ml of analytical grade dichloromethane was added to the second separation funnel, shaken for 5 minutes and allowed to stand for separation to occur. The process was repeated three times for each sample.

The extracts were pooled and dried with a spatula of anhydrous sodium sulphate and allowed to stand. Vacuum filtration using Buchner funnel and Whatman No.1 filter paper was done to remove the clumped sodium sulphate crystals from the extract. The dried sample was concentrated by rotary evaporation at 40°C to 10 ml at 4 revolutions per minute and the sample kept in amber vials at 5°C waiting clean up.

3.6.1 Clean up process

The clean up process was effected by following the EPA 3620c method. Granular anhydrous sodium sulphate was dehydrated by heating it at 400°C for 4 hours in a shallow tray using a Vulcan A-550 muffle furnace . A glass column (2 cm i.d) was packed with glass wool at the bottom then followed by a slurry of 20g Florisil in hexane using Pasteur pipette . A spatula full of anhydrous sodium sulphate was added and topped with 0.5 g of activated charcoal to remove any pigmentation. The concentrate from the extraction above was carefully added onto the anhydrous sodium sulphate layer in the column, and then eluted sequentially with 50 ml of n-hexane, followed by 200 ml of 6% diethyl ether in n-hexane, 200 ml of 15% diethyl ether in n-hexane and finally by 200 ml of 50% diethyl ether in n-hexane and the fractions collected (EPA 3620c). The third fraction was concentrated to dryness using an Eyela N-1000 rotary evaporator in a water bath temperature of 40°C. Three milliliters of HPLC grade n-hexane was used to reconstitute the analyte which was then transferred to a clean amber vial awaiting GC-NPD analysis.

3.7 Gas Chromatographic analysis of the samples

GC analysis was done at standard conditions using Varian Chrompack with NPD. The capillary column was DB-210, length 30 m, id 0.25 mm and 0.25 µm film. The carrier gas and make up gas was nitrogen with a 2 ml/min and 30 ml/min flow rate respectively. Hydrogen at 8 ml/min and air at 80 ml/min were employed in a splitless mode for the detector. 2.0 µL of the sample was injected at a temperature of 270°C. The oven temperature was kept at 120°C with a hold time of 1 minute, then from 120°C to 205°C at a rate of 25°C/min with a hold time of 1 minute and then finally from 205°C to 250°C at a rate of 1°C/min with a hold time of 1 minute. The detector was maintained at 300°C. The samples were quantified using retention time and peak area against malathion external standard of known concentration. The malathion peak was characterized by comparing the retention times with those of external standard while the degradation products were first identified using GC-MS and consequently characterized using consensus retention times.

The control and blank samples were used to calculate the recovery percentage after extraction and clean up processes as shown below:

$$\% \text{ Recovery} = \frac{Amount\ found - Amount\ from\ unspiked\ sample}{Amount\ spiked} \times 100$$

Where:

Amount found is the calculated concentration from the response of the spiked sample.

Amount from unspiked sample is the original concentration of the blank.

The recoveries ranged between 73% and 76%, showing that the extraction and clean up processes did not waste a lot of the analytes (Zweig and Devine, 1969).

3.8 Characterization of zeolites

At the end of the experiment the zeolites were dried by pressing the cake in between Whatman No. 1 filter papers and ca. 1 g of it was taken for XRD and IR analysis for characterization.

3.8.1 Infrared measurements (IR)

A mixture of 1% sample and 99% IR grade KBr (to dilute the sample for better resolution) was ground in a glass mortar to fineness. A mass of 0.10 gram of the ground mixture was pressed at 10 Ton pressure for 10 minutes. Resulting pellets were fixed in FT-IR Bruker Equinox 55 spectrometer at a nominal resolution of 2 cm^{-1}. A total of 128 scans were collected for each sample spectrum. The spectrometer was purged with nitrogen gas for 30 minutes before and after pellet insertion, after which the spectrum was recorded over the 4000 – 600 cm^{-1} range. The FTIR spectrometer was calibrated by checking the deviation between the literature and experimental polystyrene spectral band positions.

3.8.2 X-ray diffraction measurements (XRD)

The X-ray diffraction data was collected at room temperature on a Scintag XDS 2000 powder diffractometer using Cu Kα radiation of $\lambda = 1.5418$ Å with a solid state detector. The instrument settings were 40 KV, 30 mA, step size of 0.02° (2θ) and a scan rate of 2.0°/min. The XRD patterns were recorded for values of $5^{\circ} \leq 2\theta \leq 50^{\circ}$.

3.9 Data Analysis

The concentrations of malathion obtained from section 3.7 were linearly regressed to establish the relationship between concentration and time. Significant differences between the degradation products and time were established by calculation of the standard deviations. Analysis of variance was done to test significant variation ($p \leq 0.05$) between zeolite X and Y.

3.9.1 Calculations of the rate and half-life of reaction

3.9.1.1 First order reaction

Rates of chemical reactions are related to the concentrations of the reacting species. As the reactants are consumed, the rate of degradation decreases. Concentration and reaction rates therefore depend on the order of the reaction that is the number of molecules whose concentrations determine the velocity of the process (Zepp and Wolfe, 1987). For pesticides, the concentration is usually low as compared to the bulk of water and therefore the reaction can be termed a first order reaction dependent only on the concentration of the pesticide where

$$-dC/dt = kC \qquad (1)$$

Where C is concentration of pesticide

k is rate constant

t is time in hours

3.9.1.2 Calculation of the rate of reaction

Assuming a first order process, the reaction can be written as;

$$A \rightarrow B \qquad (2)$$

Then the rate law can be written as

$$-\frac{d[A]}{dt} = k\,dt \qquad (3)$$

Where [A] is concentration of species A

dt is the change in time

k is the rate constant

When integrated between the limits of time, 0 and later time t, and A_o and A;

$$\int_{[A]o}^{[A]} \frac{d[A]}{[A]} = \int_{0}^{t} dt \qquad (4)$$

This becomes

$$\ln\frac{[A]o}{[A]} = kt \qquad (5)$$

It can be written as

$$1n[A]_o - \ln[A] = kt$$

$$\ln[A] = \ln[A]_o - kt \qquad (6)$$

Consider,

$y = b + mx$ (equation of a straight line)

From (6)

$[A]_o$ – Initial concentration

$1n[A] = y$

- k = Gradient

b = ln $[A]_o$

Then a plot of ln [A] against time (t) will give a straight line that will satisfy the above condition, with the gradient k as the reaction rate constant.

3.9.1.3 Half-life calculation

Generally the rate of abiotic hydrolysis for malathion is directly proportional to the concentration of the pesticide. Assuming a first order degradation curve (Lymann *et al.*, 1990)

$$\ln C_t = \ln C_o - kt \qquad (7)$$

Where C_t is the concentration of malathion at time t

C_o is the initial concentration

k is the rate constant

A plot of ln (C_t/C_o) versus time yields a straight line with a slope equal to k. The rate constant can then be used to derive the half life $t_{1/2}$ (Wang and Hoffman, 1991)

At half-life, $C_t = ½ C_o$ (8)

Therefore equation 7 becomes

$$\ln ½C_o = \ln C_o - kt_{½} \qquad (9)$$

Equation 9 is equivalent to

$$\ln \frac{C_o}{1/2C_o} = kt_{½} \qquad (10)$$

This yields $\ln 2 = kt_{½}$, (11)

Hence $t_{½} = \frac{\ln 2}{k}$ (12)

3.9.2 Calculation of rate of reaction and half-life of n^{th} order reaction (n≠1)

3.9.2.1 Calculation of the rate of reaction

Consider a reaction

$$aA \longrightarrow \text{products} \qquad (13)$$

Then the rate law can be written as

$$\frac{-d[A]}{dt} = k[A]^n \qquad (14)$$

When integrated between the limits of time, 0 and later time t, and A_o and A;

$$\int_{[A]o}^{[A]} \frac{d[A]}{[A]^n} = -k \int_0^t dt \qquad (15)$$

This becomes

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_o^{n-1}} = (n-1)kt \qquad (16)$$

Equation 16 can be written as

$$\frac{1}{[A]^{n-1}} = (n-1)kt + \frac{1}{[A]_o^{n-1}} \qquad (17)$$

A plot of $\frac{1}{[A]^{n-1}}$ against time t, yields a straight line with gradient (n -1)k as the rate costant

3.9.2.2 Half-life calculation

At half - life, $[A] = \frac{[A]_o}{2}$ and time $t = \frac{t}{2}$

Then equation (17) becomes

$$\frac{2^{n-1}}{[A]_o} = \frac{(n-1)kt}{2} + \frac{1}{[A]_o^{n-1}} \qquad (18)$$

Equation (18) can be written as

$$\frac{(n-1)kt}{2} = \frac{2^{n-1}-1}{[A]_o} \qquad (19)$$

The half-life then becomes

$$\frac{t}{2} = \frac{2^{n-1}-1}{(n-1)k[A]_o} \qquad (20)$$

CHAPTER FOUR

4.0 RESULTS

4.1 Dissipation kinetics of malathion in lake water and its half-life

4.1.1 Dissipation kinetics of malathion and the effect of zeolites

Malathion degraded faster in the initial hours, that is almost 89% dissipation of 20 ppm malathion concentration within 6 hours (fig 3).

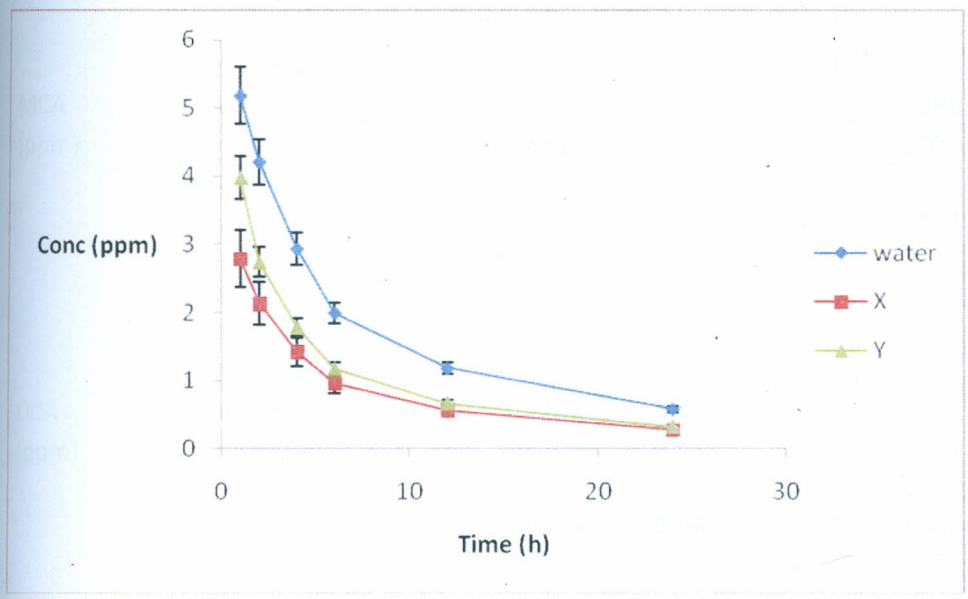


Figure 3. Malathion degradation profile
20 ppm malathion dissipation profile. Where X is water with malathion treated with zeolites X, Y is water with malathion treated with zeolites Y and water is water with malathion alone.

There after the rate of dissipation dropped significantly and was almost constant up to the detection limit of the GC (0.001ppm) at the 100th hour. With the introduction of zeolites, the dissipation rate was much faster compared to that without the zeolites. Almost 92.5% and 91% of the malathion had degraded in the initial 4 hours of the experiment in the presence of zeolite X and Y, respectively. There was significant variation ($p \leq 0.05$) between zeolite X and Y on the dissipation of malathion as shown in Table 4.

Table 4. Variation of 20 ppm malathion and its dissipation products with zeolite type and dissipation time.

		Time(h)						
		1	**2**	**4**	**6**	**12**	**24**	**mean zeolite**
Malathion	Zeolite X	2.784	2.13	1.418	0.949	0.558	0.271	1.352
(ppm)	Zeolite Y	2.932	2.207	1.458	0.97	0.567	0.274	1.401
	Mean time	2.858	2.169	1.438	0.96	0.563	0.272	
	CV%				2.57			
	LSD p≤0.05				0.052			0.149
	Interaction				0.074			
MCA	Zeolite X	0.27	0.459	0.691	1.03	0.346	0.238	0.506
(ppm)	Zeolite Y	0.402	0.532	1.003	1.325	1.037	0.021	0.72
	Mean time	0.336	0.496	0.847	1.178	0.691	0.13	
	CV%				6.79			
	LSD p≤0.05				0.062			0.176
	Interaction				0.087			
DCA	Zeolite X	0.244	0.267	0.496	0.741	1.113	1.454	0.719
(ppm)	Zeolite Y	0.193	0.303	0.518	0.781	0.81	1.208	0.635
	Mean time	0.218	0.285	0.507	0.761	0.962	1.331	
	CV%				11.2			
	LSD p≤0.05				0.112			0.322
	Interaction				0.159			
DMDTP	Zeolite X	0.134	0.141	0.132	0.034	0	0	0.073
(ppm)	Zeolite Y	0.013	0.014	0.015	0	0	0	0.007
	Mean time	0.074	0.077	0.073	0.017	0	0	
	CV%				4.11			
	LSD p≤0.05				0.045			0.128
	Interaction				NS			

MCA-Malathion monocarboxylic acid, DCA-Malathion dicarboxylic acid, DMDTP-Dimethyldithiophosphate and NS-Not Significant.

4.1.2 Half-life of malathion and effect of zeolites

The study was done within pH 7.9±0.1 and the dissipation trend tested against zeroth, first and second order kinetics with respect to the disappearance of malathion based on the concentration of malathion found in water. Since there were three time points for zeolites X and Y for the 10 ppm set, only the 20 ppm sets were used for the half-life calculation. The dissipation demonstrated pseudo first-order kinetics. (Appendix 1), and by linear regression analysis (Appendices 2-4), the first order plots gave the following reaction rates and constants as presented in Table 5

Table 5: Calculated half-lives of malathion in Lake Victoria, Kenya.

Zeolite type	Rate constant k_1 (hr^{-1})	k_2	Half-life (hours)	R^2
None	-0.144 ± 0.010	-0.104 ± 0.015	4.81	0.996
X	-0.262± 0.012	-0.179 ± 0.004	2.65	0.997
Y	-0.212± 0.019	-	3.27	0.970

R^2 value is from linear regression analysis of plot of ln (C_t/C_o) as a function of time. Rate constant is indicated as mean ± S.D (n= 3).

With the introduction of zeolites, the pH increased to 8.5±0.1 and 8.2±0.1 for zeolites X and Y respectively (Fig. 4). Malathion in water and in water with the zeolite X demonstrated bi-phasic first order kinetics (Appendix 2 and appendix 3). However, the rate constants for the second phase k_2 were much lower than k_1 (Table 5). Therefore only k_1 was used to calculate the half-lie values. In contrast malathion degradation in water with zeolite Y was monophasic (Appendix 4). The half-life of malathion in water was significantly shortened from 4.81 hours to 2.65 hours and 3.27 hours for faujasite X and Y, respectively.

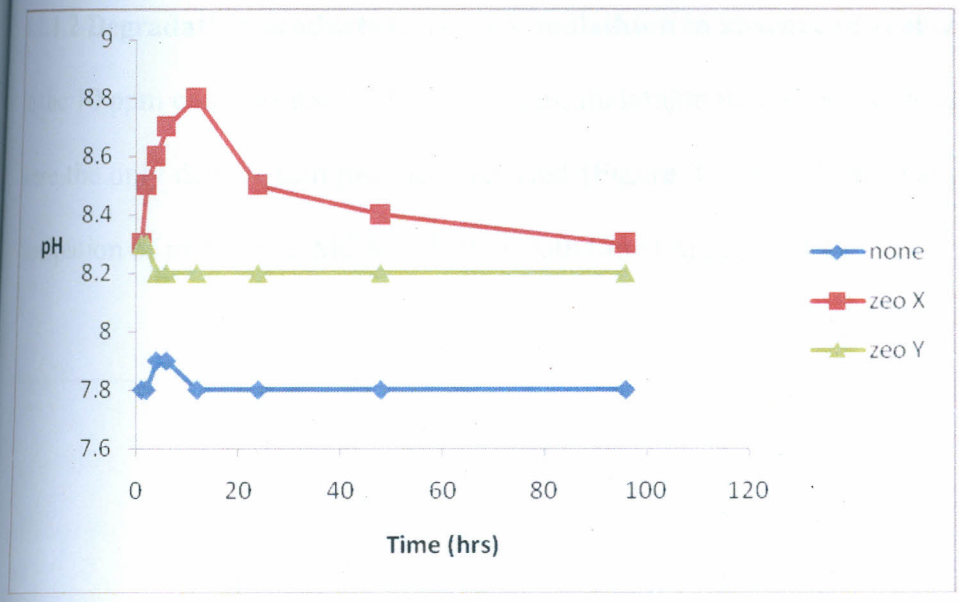


Figure 4: Change of pH with time for untreated and treated water with zeolites

In the experiments without the zeolite the pH was slightly alkaline (pH 7.9 ± 0.1) but with the introduction of the zeolite Y the water stabilized at pH 8.2 while that with zeolite X the pH dropped slowly to 8.4 and seemed to stabilize at that.

4.2 Degradation products of Malathion in water

The degradation of malathion was investigated under two initial concentrations of 10 ppm and 20 ppm with and without zeolites X and Y.

4.2.1. Degradation products of 10 ppm malathion

4.2.1.1 Degradation products of 10 ppm malathion in the presence of zeolites

The 10 ppm concentration in the presence of zeolites had minimal malathion residues and no other degradation products were detected.

4.2.1.2 Degradation products of 10 ppm malathion in absence of zeolites

In the 10 ppm concentration without zeolites, malathion monocarboxylic acid and the dicarboxylic acid were the only degradation products detected (Figure 4). Significant variation ($p \leq 0.05$) existed in the dissipation of malathion, MCA and DCA with time (Appendix 12).

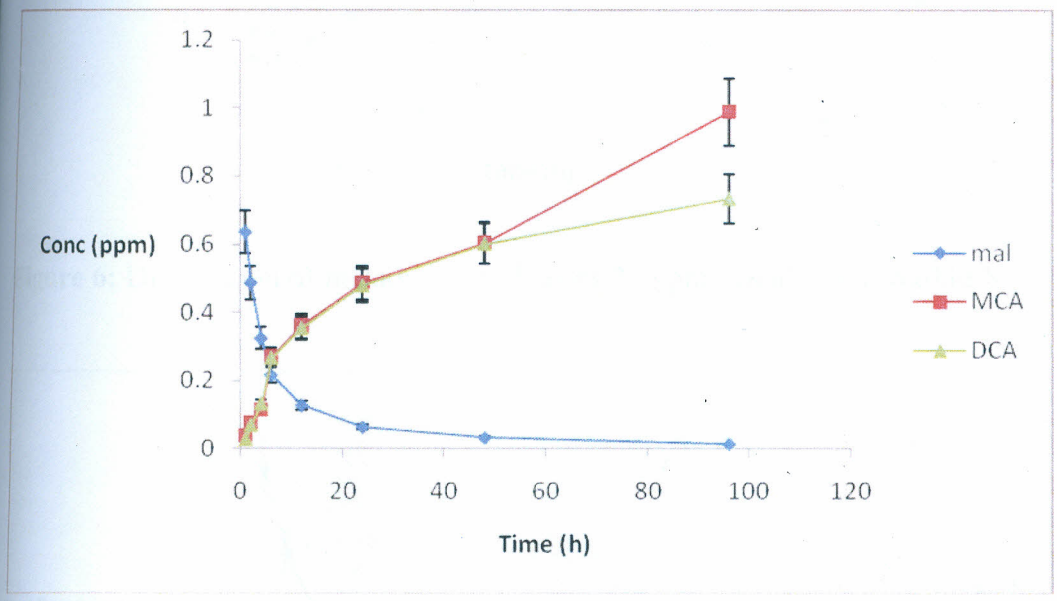


Figure 5: Distribution of degradation products of 10 ppm malathion without zeolites where MCA is malathion monocarboxylic acid, DCA is malathion dicarboxylic acid and Mal is malathion.

4.2.2 Degradation products of malathion with zeolite

Upon introduction of the zeolites, besides MCA and DCA, another degradation product was detected: dimethyldithiophosphate (DMDTP) though in minimal concentrations as compared to the other two. In zeolite X (DMDTP) was detected up to the sixth hour (Figure 6 and appendix 6) while in zeolite Y it was only detected up to the fourth hour (Figure 7 and appendix 7).

Since DMDTP was only detected upto the sixth hour only, it had a large CV% and a squareroot transformation had to be done on its data (Appendix 11). There was significant variations ($p \leq 0.05$) in DMDTP dissipation rate at each time using the two zeolites but the dissipation pattern was the same for both zeolites.

4.3 Efficiency of zeolites in the degradation of malathion

Malathion, both 10 and 20 ppm, rapidly dissipated in the initial hours from the start of the experiment forming the three products detected and followed by a slower second phase. With the introduction of the zeolites, the dissipation was made faster. With the 10 ppm concentration in the presence of zeolites, malathion could not be detected after the forth hour whereas without the zeolites degradation went on upto the 96th hour (Table 6). In the initial four hours the treatment without the zeolites had degraded almost 98% of malathion while those with zeolite had almost 100%. Zeolite X had higher percentage recoveries as compared to zeolite Y.

Table 6: Percentage malathion residue from 10 ppm concentration in water

Time(hrs)	Water(ppm)	X+water(ppm)	%X removal	Y+water(ppm)	Y% removal
1	0.635± 0.017	0.078 ± 0.007	56.22	0.402 ± 0.133	36.69
2	0.486± 0.008	0.067 ± 0.002	57.85	0.257 ± 0.111	39.43
4	0.323± 0.091	0.057 ± 0.006	58.85	0.237 ± 0.167	42.63
6	0.216± 0.054	BDL	NC	BDL	NC
12	0.127± 0.009	BDL	NC	BDL	NC
24	0.063± 0.059	BDL	NC	BDL	NC
48	0.032± 0.012	BDL	NC	BDL	NC
96	0.013± 0.102	BDL	NC	BDL	NC

All the concentrations are expressed as (ppm ± S.D) where n=3

Likewise, for the 20 ppm there was rapid initial degradation for the first hour though not as fast as the 10 ppm experiment. Similarly, zeolite X showed slightly higher percentage removal of malathion residue with time as compared to Y (Table 7).

Table 7: Percentage malathion residue from 20 ppm concentration in water

Time(hrs)	Water (ppm)	X+water (ppm)	%X removal	Y+water (ppm)	Y% removal
1	5.175 ± 0.043	2.784 ± 0.082	46.21	3.977 ± 0.043	23.15
2	4.212 ± 0.049	2.130 ± 0.098	49.43	2.732± 0.049	35.14
4	2.934 ± 0.114	1.418 ± 0.091	51.67	1.779 ± 0.114	39.37
6	1.985 ± 0.060	0.949 ± 0.104	52.19	1.168 ± 0.060	41.16
12	1.182 ± 0.031	0.558 ± 0.104	52.79	0.674 ± 0.031	42.98
24	0.577 ± 0.010	0.271 ± 0.028	53.01	0.317 ± 0.010	45.06
48	0.237 ± 0.021	BDL	NC	BDL	NC
96	0.095 ± 0.017	BDL	NC	BDL	NC

All the concentrations are expressed as (ppm ± S.D) where n=3

BDL-below Detection Limit NC-Not Calculated

4.4 X-ray diffraction (XRD) of the zeolites

4.4.1 X-ray diffraction for zeolite X

The exposure of zeolite X to malathion decreased the relative intensities of the diffractograms at 9.9° (2θ) from 3361 a.u to 1460 and 1519 a.u for 10 and 20 ppm respectively. While those at 11.6° (2θ) increased from 834 a.u to 1185 and 1195 a.u for 10 and 20 ppm respectively, as shown in Figure 8.

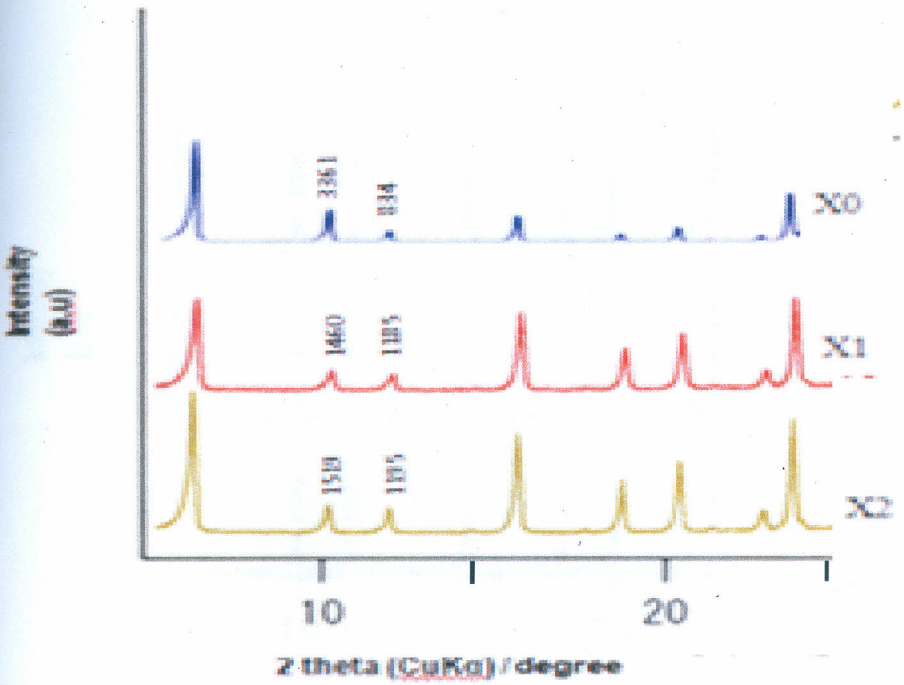


Figure 8: The XRD spectra for zeolite X in malathion where X0 = Hydrated zeolite X with 0 ppm malathion, X1= Hydrated zeolite with 10 ppm malathion, X2= Hydrated zeolite X with 20 ppm malathion

4.4.2 X-ray diffraction for zeolite Y

Exposure of malathion to zeolite Y decreased the relative intensities of the diffractograms at 11.7° (2θ) from 728 a.u to 650 and 962 a.u for 10 and 20 ppm concentrations respectively, while at 9.9° (2θ) the intensity increased from 1036 a.u to 1179 a.u for the 20 ppm concentration as seen in Figure 9.

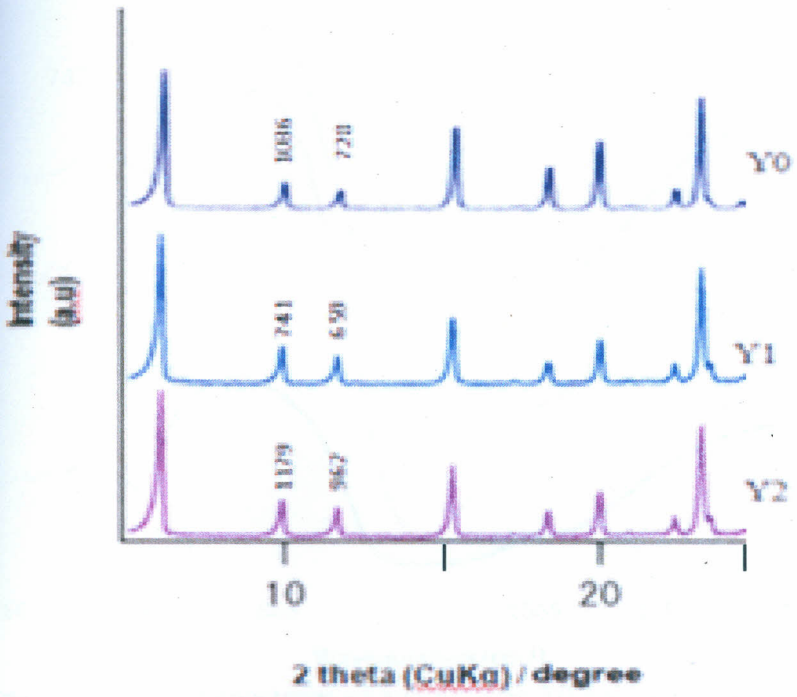


Figure 9: The XRD spectra for zeolite Y in malathion where Y0 = Hydrated zeolite Y with 0ppm malathion, Y1= Hydrated zeolite Y with 10 ppm malathion, Y2= Hydrated zeolite Y with 20 ppm malathion.

4.5 Infra-red analysis of zeolites

From the infra-red analysis, the mid infra-red region (1250-650 cm^{-1}) is informative in characterizing the framework of zeolites under consideration.

4.5.1. Infra red analysis of faujasite X

The characteristic band of hydrated Faujasite X appeared at 764cm^{-1}. With the introduction of faujasite X to 10 ppm malathion, there was a shift of the S4R from 764 cm^{-1} to the lower frequency of 744 cm^{-1} for hydrated zeolite X (Figure 10). For the 20 ppm malathion concentration there was a minimal shift to 742 cm^{-1}.

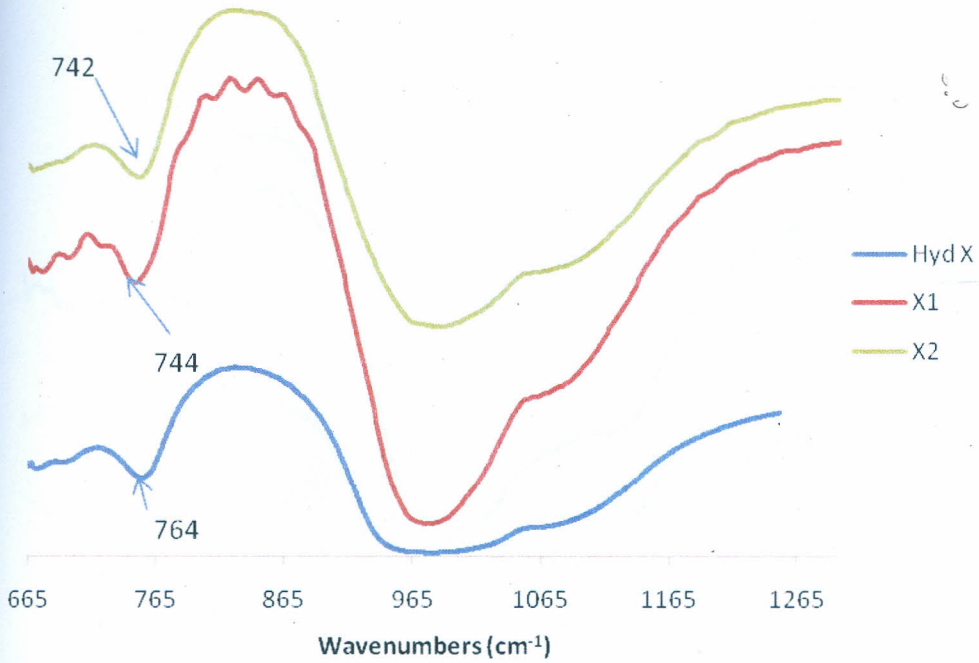


Figure 10: Infra-red spectrum of zeolite X in 10 ppm and 20 ppm Malathion where Hyd X is hydrated X, X1 is 10 ppm malathion in zeolite X and X2 is 20 ppm malathion in zeolite X.

4.5.2. Infra-red analysis of Faujasite Y

With introduction of malathion to hydrated Y type zeolites, there was a shift of S4R from 781 cm^{-1} band to the higher frequency bands of 796 cm^{-1} and 795 cm^{-1} for the 10 ppm and the 20 ppm concentrations respectively.

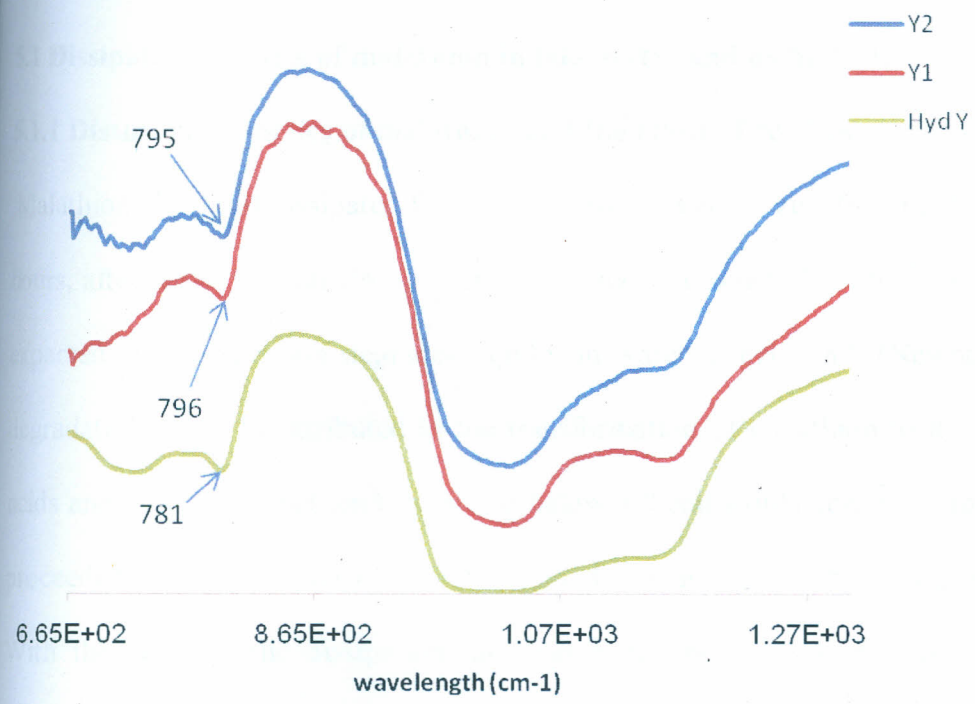


Figure 11: Infra-red spectrum of zeolite Y in 10 ppm and 20 ppm malathion where Hyd Y is hydrated Y, Y1 is 10 ppm malathion in zeolite Y and Y2 is 20 ppm malathion in zeolite Y.

CHAPTER FIVE

5.0 DISCUSSION

5.1 Dissipation kinetics of malathion in lake water and its half-life

5.1.1 Dissipation kinetics of malathion and the effect of zeolites

Malathion (20 ppm) dissipated faster in lake water without zeolite with 89% dissipation in the initial 6 hours, after which the rate dropped and was almost constant to the 96th hour (Figure 3). This trend was expected since malathion degrades rapidly in water at pH > 8.0 (Newhart, 2006). The initial rapid degradation could be attributed to the transformation of malathion to its products which are majorly acids and as such the pH tends to fall to below 8.0 and would continue dropping as the transformation proceeded and thus this slows down the degradation as reported by Zheng and Hwang, 2006.

With the zeolites, the dissipation rate was much faster compared to the experiments without the zeolites. This increased dissipation was attributed to a combination of two factors: high pH effect and catalytic action that lead to faster degradation and/or adsorption of the zeolites (Maxwell, 1982). Since the pH increased when zeolite was added, faster initial degradation was expected due to high pH effect which generally enhances the degradation of malathion (Newhart, 2006). As much as there was increased degradation with introduction of the zeolites, zeolites X was faster than the Y (Figure 3). This is explained by the fact that in alkaline conditions, the high silica zeolites (zeolites Y) show decreased base stability as compared to the low silica zeolites (zeolites X) (Riberin and Rodriguez,1984). This therefore means that zeolite X catalysis is highly favoured in such conditions. Besides, the alkaline nature of the zeolites, they also possess catalytic properties. Thus the two factors combined contributed to the faster dissipation rate (Satterfield, 1980).

5.1.2. Half-life of malathion and the effect of zeolites

As much as the data was consistent with second order kinetics from regression analysis (Appendix 1), pseudo first order approximation was adopted since water, which was the source of the second reactant (OH^- ions) was present in great amounts compared to malathion, that any change in OH^- ions would be negligible. Because of its abundance, OH^- ions cannot be rate limiting. The reaction is then a solvolysis reaction (Isaacs, 1987) whose rate is more dependent on the concentration of malathion alone. The calculated half-life of malathion, by application of equation 12 in untreated water, was found to be 8.76 hours (Table 4). This half-life was found to be shorter when compared to other values in literature. For instance, Wang and Hoffman (1991) reported a half-life of 2 days for malathion in river water in the dark at pH 8.2 and 28°C. Neal *et al.*, (1993) also reported a half-life of 2 days but under unspecified conditions. Freed (1979) reported freshwater half-life value for malathion as 11 days at pH 7.4 and a temperature of 20°C. The differences in the half-lives could be attributed to the different locations since the reported works were carried out in the temperate regions while this study was done in the tropics (Zheng and Hwang, 2006). Also photolysis and volatilization may have shortened the half-life since the reported studies were done in the dark as compared to the current study which was performed under room temperature and light conditions.

With the zeolites, the half-life of malathion was shortened from 4.81 hours to 2.65 hours and 3.27 hours for zeolites X and Y, respectively (Table 4). This reduction is in agreement with past studies that indicated zeolites are capable of enhancing the degradation of pesticides. Osewe (2010) reported enhanced degradation of DDT from a half life of 56 days in fresh lake water to 6.1 hours and 9.6 hours for zeolite X and Y respectively in the tropical region. Yang *et al.*, (2006) also reported significant decomposition of DMMP in the presence of zeolites. The enhanced degradation of malathion by zeolites is because of their catalytic nature since zeolites have exchangeable cations, allowing the

introduction of cations with various catalytic properties into their cavities (Gates, 1979; Satterfield, 1980). Since faujasite X has more exchangeable cations in its cavities than faujasite Y, its reaction is therefore expected to be faster than the Y type as was found in the current study.

5.2. Degradation products of Malathion in water

The major degradation products of malathion in water detected in the current study are the malathion mono and dicarboxylic acids. This is in agreement with the studies done by Lalah and Wandiga (2002) and Howard (1991) who reported that during the transformation of malathion in water, the major metabolites of malathion include malathion α- and β- mono-carboxylic and malathion dicarboxylic acid. Metabolites detected from the experiments with zeolites had malathion α- and β- mono-carboxylic and malathion dicarboxylic acids as the major degradation products but also DMDTP as also detected though in minimal quantities (Fig 6 and 7). In zeolite X it was detected up to the sixth hour (Figure 6) while in zeolite Y it was only detected up to the fourth hour (Figure 7). The failure to detect DMDTP in water alone could be attributed to the fact that the pH was lower in the initial hours when compared to the treatments with zeolites (Figure 4) where it was detected. Metabolites of hydrolysis of malathion also include malaoxon, diethyl fumarate, diethyl thiomalate, O, O-dimethylphosphorodithioic acid, diethyl thiomalate and O, O-dimethylphosphorothionic acid (Newhart, 2006). Wolfe et al, (1975) also reported O, O-dimethylphosphorodithioic acid as a metabolite of malathion in water. In alkaline medium, the salt of dimethyldithiophosphoric acid and an ester of fumaric acid are formed. Transformation of malathion essentially depends on the pH; as such the metabolites differ in acidic and alkaline conditions (Zheng and Hwang, 2006).

The change of pH with time (Figure 4) could have led to the difference in the degradation products in the experiments with and without the zeolites. Montgomery (2007) reported that hydrolysis products

are dependent on pH. In alkaline solutions malathion hydrolyses to form diethyl fumarate and dimethyl phosphorodithioic acid (Bender, 1969).

DCA increased with time in all experiments as the concentration of malathion decreased. This was expected since it is the hydrolysis of malathion that leads to formation of MCA and DCA which are the major degradation products of malathion (Lalah and Wandiga, 2002). MCA increased from the start to the sixth hour then started decreasing, this is attributed to the sorption-desorption by the zeolites (Yang *et al.*, 2006) and also due to the formation of DCA.

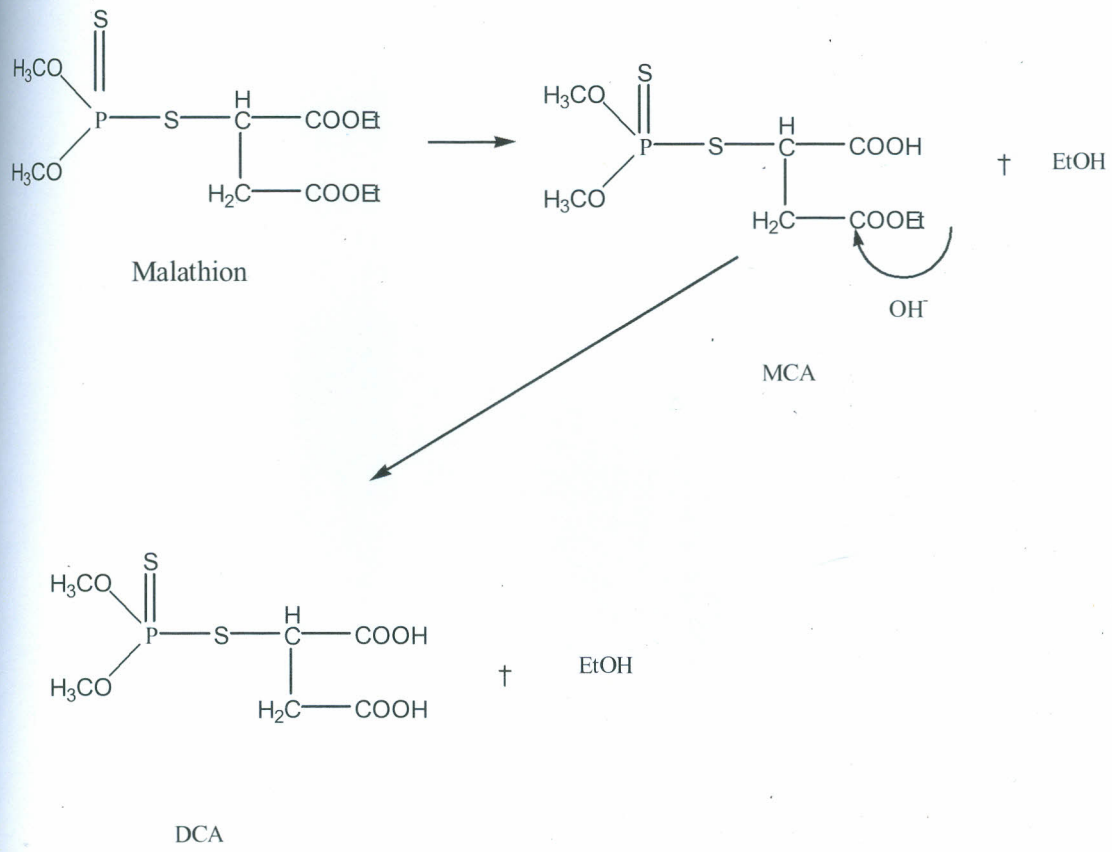
The degradation products (MCA, DCA and DMDTP) realized from these experiments have much lower toxicity levels than malathion itself and other degradation products of malathion in water (see scheme 2). Malaoxon being the most toxic of the degradation products of malathion as shown in Table 2, was not detected from these experiments since it is usually formed under biodegradation (Newhart, 2006) which was not the case in this study.

Significant variations between the two zeolites (Table 4), suggests that the rate of degradation/dissipation of malathion and the detected products in the presence of the two is not the same moving from one time to the other. Also the pattern of degradation/dissipation of malathion and its products in the two zeolites was not the same apart for DMDTP where the pattern was the same.

5.3 Mechanism of Malathion degradation in water

Malathion mainly undergoes hydrolysis in water (Wolfe *et al.*, 1977) with a pH value of 4 or greater and the degradation rate increases proportionately with pH. On the other hand, the pH values of this hydrolysis experiments were high (pH of 7.8-8.4)(Figure 4); hence, there was abundant supply of nucleophiles such as OH^- in the solution and the nucleophilic attack by the surface coordinate hydroxide ions became less important (Hong and Pehkonen, 1998). For this study, the probable

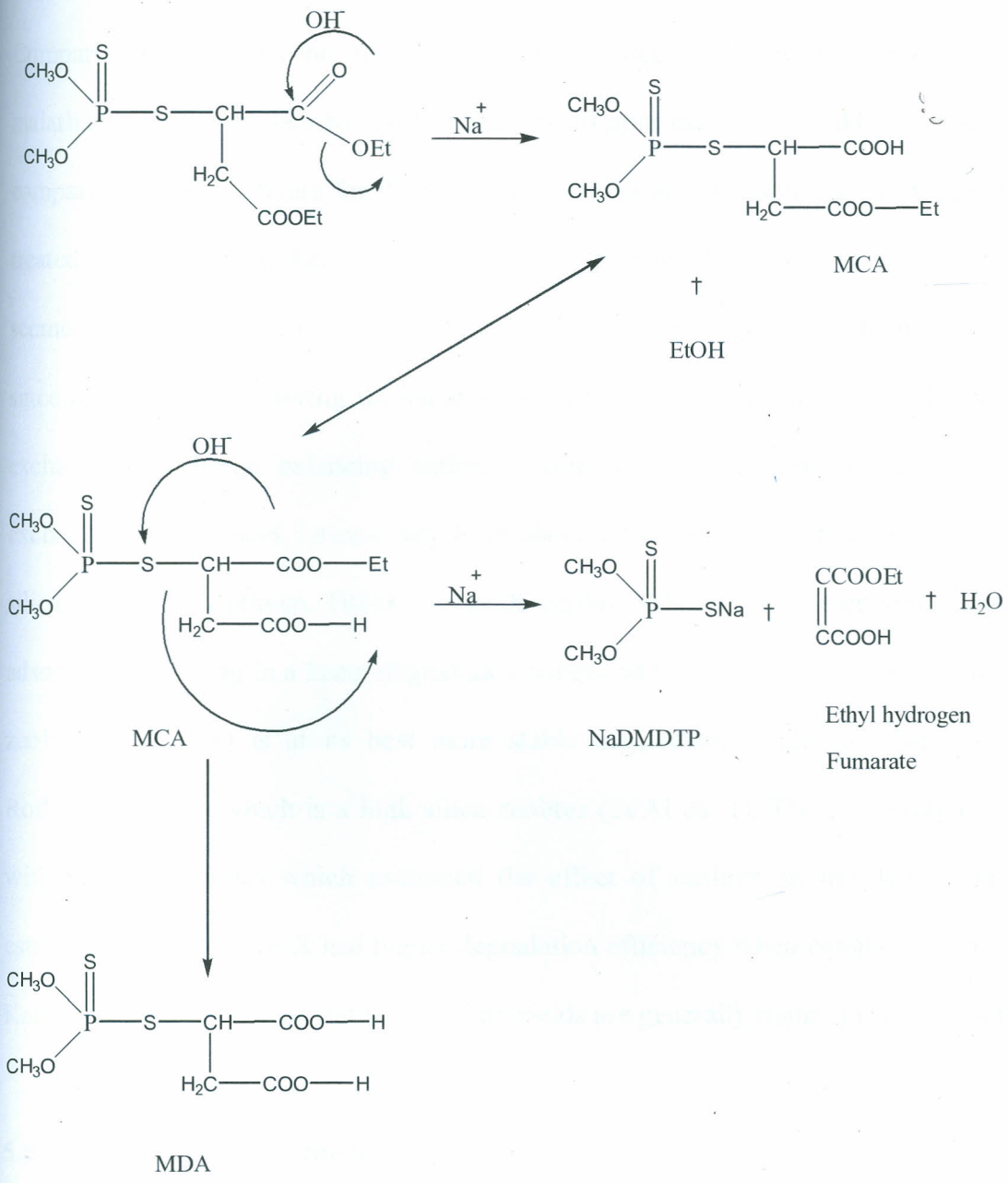
mechanism of degradation is hydrolysis and biodegradation because the loss caused by volatilization was relatively minimal since the jars were corked. For the experiment without the zeolites, the only hydrolytic products detected were the malathion α- mono and di-carboxylic acids (scheme 3). This mechanism is basically hydrolysis of the two ethyl esters attached to the S-C bond which according to Chen *et al.*, (1969) leads to the formation of either α-MCA exclusively or including DCA.



Scheme 3: Proposed mechanism for the hydrolysis of malathion without zeolites

For the treatments with the zeolites, besides the mono-carboxylic and di-carboxylic acids, O, O-dimethyl phosphorodithioate was also identified in the two zeolites though in minimal amounts (Scheme 4). This is a product of the hydrolysis of the P-S-C bond at an alkaline pH (Getenga, 1999). The nucleophile in this case is OH^- which is several orders, specifically 10^8 stronger than water

(Barnard *et al.*, 1961). The initial hydrolysis product is the malathion mono-carboxylic acid which still undergoes further hydrolysis although at a slower rate (Hong and Pehkonen, 1998) to form DMDTP and malathion di-carboxylic acids as the other hydrolysis products. Although DMDTP is identified as a product, it is a minor one compared to the carboxylic acids. In this study, it was only detected after the second hour and up to the eighth hour at most (Figure 5 and 6). In alkaline conditions hydrolysis of malathion yields $(CH_3O)_2P(S)Na$ and $(CH_3O)_2P(S)OH$ (Sittig, 1985)



Scheme 4: Proposed mechanism for the degradation of malathion in the presence of zeolites. Where MCA is malathion monocarboxylic acid, MDA is malathion dicarboxylic acid and DMDTP is Dimethyldithiophosphate.

5.4 Efficiency of zeolites in the degradation of Malathion

Comparing the two concentrations, zeolites seem to degrade faster the 10 ppm than the 20 ppm malathion. This is evident by the fact that for 20 ppm malathion could not be detected after 24 hours compared to only 4 hours for the 10 ppm concentration. It is evident from Tables 6 and 7 that water treated with the zeolite had malathion degrading faster than that without. On comparison, zeolite X seemed to be more efficient in enhancing the degradation of malathion than zeolite Y. This is expected since despite the two having the same physical properties, zeolite X unit cell contains 86 monovalent exchangeable charge balancing cations, while the Y cell contains only 56 of such ions. The exchangeable univalent cations vary from about 10-12 per cage for zeolite X to as low as 6 for high silica zeolite Y (Ruthven, 1984). As such, zeolite X has a larger electronic charge for catalysis and adsorption resulting in a faster degradation compared to zeolite Y. Also the X zeolite being a low silica zeolite (Si/Al=2-5) is at its best more stable in alkaline conditions than zeolite Y (Riberin and Rodriguez, 1984) which is a high silica zeolites (Si/Al ca. 1). This observation is strongly correlated with previous studies which examined the effect of zeolites on the degradation rate of DDT and established that zeolites X had higher degradation efficiency when compared to Y (Osewe, 2010). Also Kanyi *et al.*, (2006) found out that product yields are generally higher in zeolites X than in the Y type.

5.5 X-ray diffraction of the used zeolites

5.5.1. X-ray diffraction of used zeolite X

The XRD analysis further proved that zeolite X has better catalytic and/ or adsorption properties than the Y type. Only two reflections showed high concentration of sodium ion as compared to the others. From the XRD results in Figure 8, zeolites X has better catalytic properties than the Y. The relative increase in the peaks at 11.6^{o} (2θ) are consistent with the Na^{+} migrating from the zeolite framework

into the void spaces (Kowenje *et al.*, 2010). This observation is expected as there is an abundance of exchangeable Na^+ in zeolite X corroborating the proposed mechanism in scheme 4. The presence of many cations in the void spaces acts as catalysts therefore the degradation process is faster in X compared to the faujasite Y. Osewe (2010), also reported the increase in the peaks at ca. 11.6° (2θ) from the faujasite X treatment in DDT degradation. Salama *et al.*, (2006) also observed that the reversal of the XRD peaks corroborates the redistribution of copper ions from one site , possibly the sodalite to another possibly the supercage.

5.5.2 X-ray diffraction for zeolite Y

It appears the effect of migration of exchangeable Na^+ is less noticeable at 10 ppm malathion experimental level but more appreciable at 20 ppm (Figure 9). Since Y zeolite has fewer Na^+, the observation points to a Na^+ mediated mechanism though the process is much slower than the faujasite X due to fewer cations in the void spaces.

This difference in Na^+ concentration between X and Y would explain the observed difference in the DMDTP concentrations between X (Figure 6) and Y (Figure 7) treatments. Due to abundance of Na^+ in X, the concentration of DMDTP was higher in the X than the Y implying that the degradation was Na^+ mediated.

5.6 Infra red analysis of Faujasite zeolites

5.6.1. Infra-red analysis of Faujasite X

With introduction of malathion, the single four rings (S4R) symmetric stretching mode shifted from 764 cm^{-1} to lower frequency side of the strongest band (Figure 10). The shift of the band towards the

lower frequency side with introduction of malathion can be explained on the basis of Hooke's law (Silverstein *et al.*, 1981), which is stated as;

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

where $\bar{\nu}$ is the vibrational frequency (cm^{-1}) , c is the velocity of light (cm/s), k is the stretching force constant (dynes/cm) and μ is the reduced mass (g). During the process of ion exchange, and with the introduction of malathion molecules, the reduced mass increases leading to a decrease in the vibrational frequency. This attachment is more possible in faujasite X since it has a higher nucleophilicity compared to faujasite Y therefore there is a probable formation of methoxy groups in the cages (Kanyi *et al.*, 2006). The presence of Na^+ in the supercage site III (see Figure 3) in X type zeolite stabilizes the transition state of the nucleophilic substitution reaction.

5.6.2. Infra-red analysis of Faujasite Y.

The blue shift observed with introduction of 10 and 20 ppm concentrations of malathion to Faujasite Y is due to the reduction of mass from the Hookes law. The shifting implies that there was loss of cations from the sites but resulted in little attachment if any, of the organic moeity into the sites. This observation is true since due to the nature of the Y type zeolite, the comparative paucity of site III Na^+ does not provide this kind of stabilization as it does for NaX for the formation of the framework alkoxy species in NaY (Kanyi *et al.*, 2006).

CHAPTER SIX

6.0. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1. Summary

This study sought to establish the effects of the zeolite on the degradation and elimination of the pesticide malathion from fresh water. The study investigated two types of zeolites, faujasite X and Y under three different concentrations (0, 10 and 20 ppm) of malathion spiked in water. From the data presented in this report and those from shown literature elsewhere, the following summary can be made.

1. The half-life of malathion in fresh water from Lake Victoria within a pH 7.9±0.1 was found to be 4.81 hours. With the introduction of the Faujasite zeolites the pH increased to 8.5 and the half-life under zeolite X treatment was 2.65 hours whereas under zeolite Y it was found to be 3.27 hours.
2. Malathion degradation in fresh water was found to undergo pseudo- first order kinetics (R^2= 0.996) with a rate constant of -0.144±0.010 hr^{-1}. On addition of both faujasite zeolites the kinetics was also found to be pseudo-first order (R^2= 0.997, 0.970) with rate constants of -0.262±0.012 and -0.212±0.019 hr^{-1} for X and Y, respectively.
3. Malathion degraded in water to form malathion α and β mono-carboxylic acid and malathion dicarboxylic acid as the products. With the zeolites treatment, 10 ppm concentration had minimal malathion residues with no any other degradation products whereas in the 20 ppm concentration besides malathion mono and dicarboxylic acids, dimethyldithiophosphate was also detected in both faujasite X and Y treatments.
4. Malathion majorly underwent hydrolysis in water as the mechanism of degradation as shown by the type of metabolite formed. In this case the two ethyl esters attached to the S-C bond were

hydrolysed to malathion monocarboxylic acids and the dicarboxylic acid. With addition of the faujasite zeolite the mechanism was also hydrolysis at the P-S-C bond under alkaline condition to form the malathion acids and DMDTP.

5. Faujasite X was found to have a higher percentage in the degradation of malathion compared to the faujasite Y though both the zeolites had higher percentages in degradation when compared to malathion degradation in water alone.

6.2 Conclusions

With the respect to the summary above, the null hypothesis was adopted and the conclusions therefore are;

1. Faujasite zeolites were found to enhance the degradation of malathion in water although the X type was faster than the Y type.
2. Malathion degradation, in fresh water and fresh water with zeolites, undergoes pseudo-first order kinetics.
3. Malathion degradation in fresh water and in the presence of zeolites produces malathion mono- and malathion di-carboxylic acids as well as dimethyldithiophosphate as the degradation products.
4. The major mechanism of degradation of malathion in fresh water and fresh water with zeolites is hydrolysis at the P-S-C bond of malathion.
5. Faujasite X is more efficient in enhancing the degradation of malathion in fresh water as compared to the faujasite Y.
6. Lower concentrations are easily degraded with the zeolites compared to higher concentrations.

6.3. Recommendations

1. The faujasite zeolites should be incorporated in water treatment plants since they are capable of enhancing the degradation of malathion.
2. As much as the faujasites enhance the degradation of malathion, faujasite X should be encouraged for use since it is more efficient thus more economical.
3. Other zeolites should be investigated for their degradation actions on pesticide
4. Other groups of pesticides should be investigated for their degradation in the presence of zeolites.
5. A study should be carried out to determine the efficient amount of zeolite to use per litre of water.
6. In line with number 5 above, a study should be carried out to determine how long the zeolite would be efficient before replacing.

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