THE EFFECTS OF ZEOLITE X AND Y ON DEGRADATION KINETICS OF p,p'-DICHLORODIPHENYLYTRICHLOROETHANE (DDT) IN NATURALWATER

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ABSTRACT

The study was on degradation kinetics of pesticides in water by zeolites. Pesticides are never target specific and as such, aerial dissipation of pesticides is potentially hazardous to man and environmental biodiversity. Pesticide residues are in addition dispersed in the environment mostly through agricultural runoff, industrial and domestic effluent. The use of pesticides inevitably leaves behind residues in main domestic water sources. Man thus has had adverse health effects through the consumption of water from these sources. Current water purification in use lacks the capacity to get rid of most pesticides and their degradation products.

Research done in Belgrade – Montenegro had reported that the presence of some zeolites in the wastewater enhances the degradation of pesticide contaminants. However data on degradation kinetics of pesticides in the presence of zeolites is lacking, as there is no work documented. The study of this pesticides i.e., organochlorides as represented by DDT, was therefore justified as the results have proved that zeolite is capable of enhancing pesticide degradation. The study was necessitated by the fact that water bodies act as reservoirs of what remains after plants and soil accumulate the said pesticides and their breakdown products.

The broad objective was to have zeolite as a cheaper and reusable drinking water cleaning agent capable of enhancing pesticide degradation during water treatment. The activities of the project included; purchase and dehydration of the zeolites, exposing various concentrations of pesticides in water containing known concentrations of zeolites. Sample water used was taken from Kisumu City at the shore of Lake Victoria. Chemical analysis of residues of pesticides was done by GC-ECD and GC-MS. Various experimental set ups were made to enable the study of the

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three aspects mentioned above and ANOVAs (students'- test) was used to show variations

In this study, activated Faujasite –X and –Y Zeolites were separately exposed to different concentrations of 1, 1 – (2, 2, 2 – dichloroethyldiene) bis(4 – chlorobenzene) (Dichloro dipheny trichloroethane - DDT) water solutions. For the DDT solutions of <10 ppm, the resultant degradation products and residual DDT were minimal. Those of ≥ 10 ppm, the Faujasite-X and -Y media showed an initial DDT degradation half-life of approximately 6.1 hours and 9.6 hours respectively. The main degradation product in the Faujasite – X was Dichloro diphenyl dichloroethylene (DDE) whereas in the Faujasite – Y, considerable amounts of both DDE and Dichloro diphenyl dichloroethane (DDD) were obtained. The information obtained furthered scientific knowledge on effectiveness of zeolite to enhance pesticide residue degradation in water. The information can be used by various environmental authorities and municipal water treatment bodies to enhance the quality of drinking water.

CHAPTER ONE

1.0 INTRODUCTION

1.1 General

The primary purpose of water treatment is to separate the pollutants from the water or degrade pollutants to harmless residues and therefore make the water fit for intended usage. The pollutants can be partially removed by biological treatment whose aim is to lower the pathogenic count of microorganisms in the water or by other physical decontamination methods. Kenya, being a country whose economy highly depends on agricultural activities, advocates for the use of pesticides in agriculture to mitigate pests and thus make the water bodies to be highly contaminated with the pesticide residues.

1.2 Zeolites

The word zeolite stems from the Greek word 'zeo' (boiling) and 'litos' (stone). More than one hundred and eighty structures of zeolites have been identified while great progress has been gained in the synthetic zeolites mainly by Linole and Mobile Company (Gates et al., 1979). Zeolites have the following properties; Open cage like structures, high cation exchange capacities, high internal and external surface areas, variable aggregate sizes and high permeabilities.

1.3 Nature of Zeolites

Zeolites can be defined as an aluminosilicate with frame work structure (Figure 4) enclosing cavities occupied by large cations and water molecules both of which have freedom of movement and reptation, permitting ion exchange and reversible dehydration (Smith, 1993). These structures consist of corner-linked tetrahedral in which small atoms (denoted as T) lie at the centre (dominated by Al and Si atoms) and are chemically related to atoms such as Ga, Ge and P which are incorporated in

the synthetic zeolites and oxygen atoms lie at the corners (American chemical Society, 1976). The tunable chemical properties of zeolites have been known to depend on their Si/Al ratio and levels of cation exchange (Kowenje et al., 2006).

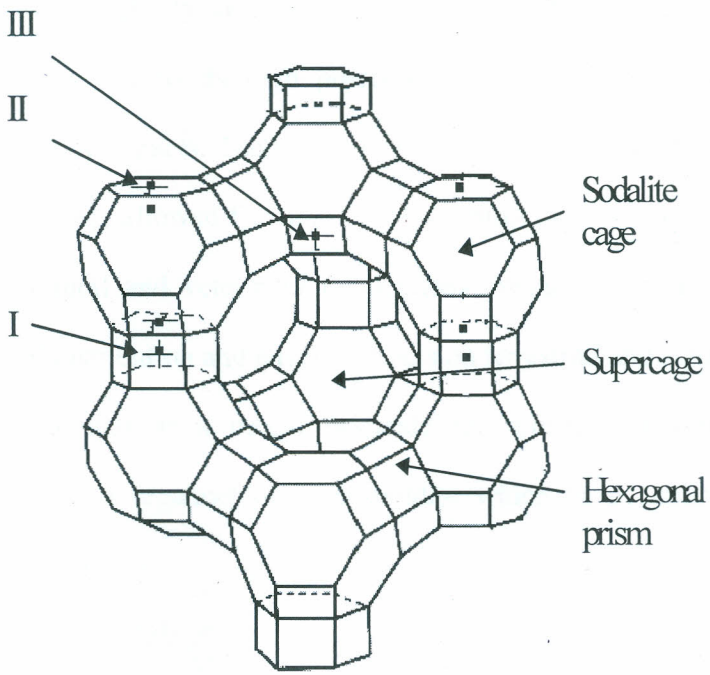


Figure 1. Faujasite-zeolite cages and the cation exchange sites (I – III). (Adopted from international Zeolite Association; www.IZA.com)

1.4 Statement of the problem

The current water treatment processes do not eliminate or are not effective in removing completely the pollutants of pesticide residue nature. However, human beings especially need clean water free of these pesticide residues in domestic water. To avoid this therefore necessitates the search for an effective procedure of water treatment that can eliminate these pesticide residues through adsorption and probably enhance their degradation to less harmful or harmless residues. The current study was therefore destined to test the possibility of using various zeolites to achieve this notable goal.

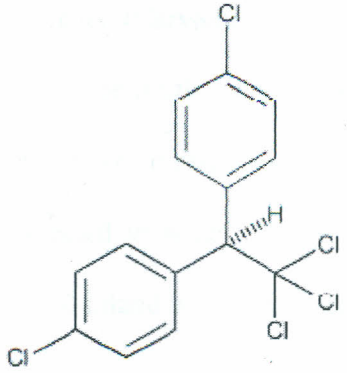
1.5 Dichlorodiphenyltrichloroethane (*p, p'*-DDT)

Dichlorodiphenyltrichloroethane (*p, p'*-DDT) usage has had a profound effect in the history of pest control owing to its low costs, broad spectrum of activity, high residual biological activity and ease of formulation (Stickle, 1974). It is banned in most countries due to its high presence in the environment and subsequent negative ecological impacts. The use of *p, p'*-DDT in Kenya has been banned since 1997 but restrictively allowed for public health control purposes only, however it is banned for agricultural and veterinary applications (Wandiga, *et. al.,* 1996). Due to its wide global distribution and adverse effects on terrestrial and aquatic life, *p, p'*-DDT is still very popular as a model pesticide for scientific investigations on environment behavior of organochlorine pesticides, which have similar physical and chemical properties.

Table1.Physical Properties of *p, p'*-DDT.

Molecular Weight:	354.51
Water solubility:	< 1 mg/L at 20 ^{O}C
Solubility in solvents:	Cyclohexanone v.s., dioxane v.s., benzene v.s., xylene v.s., trichloroethylene v.s., dichloromethane v.s., acetone v.s., chloroform v.s., diethyl ether v.s., ethanol s. and methanol s.
Melting Point:	108.5-109°C
Vapor Pressure:	0.025 Mpa at25^{O}C

Figure 2. Structure of *p, p'*-DDT



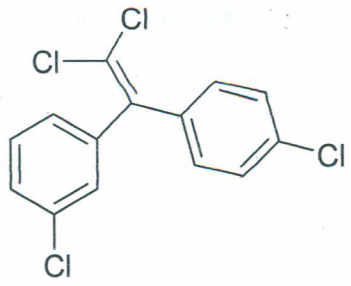


Figure 3. The structure of Dichlorodiphenyltrichloroethylene (*p, p'*-DDE).

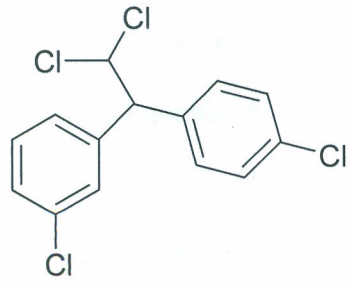


Figure 4. The structure of Dichlorodiphenyltrichloroethane (*p, p'*-DDD)

Recent evidence shows that *p, p'*-DDT and other organochlorine pesticides can degrade much more rapidly in the tropics than in the temperate regions (Wandiga, 1996). This enhanced degradation has been attributed to climatic and ecological factors which include high tropical temperatures, intense ultraviolet radiation and different physico-chemical and biological soil properties which enable processes of volatilization, photo-decomposition and microbial degradation to occur more rapidly under tropical conditions. In fact, it has now been reported that tropical climatic and ecological conditions favor more rapid degradation of pesticides in soil and aquatic environments (Carvalho et al., 1992; Lalah et al., 1994). However, residues of organochlorine pesticides such as *p, p'*-DDT, endosulfan, aldrin, endrin, dieldrin and lindane that are transported from the point of application by wind and water, have been detected in water, sediment, fish and other aquatic organisms obtained from coastal and inland waters of many tropical countries (Biddleman et al., 1973; Lalah et

al., 2003). Studies conducted in Kenya reported the presence of lindane, aldrin, endosulfan, *p, p'*-DDE, dieldrin, *p, p'*-DDT residues in seawater, seaweed, sediment and fish samples collected from different sites near Mombasa along the Indian Ocean coast with higher concentrations in samples taken during the rainy seasons compared to those taken during the dry periods (Barasa, 1999). These residues have also been found in sediment samples collected from the inland Lakes of Baringo, Naivasha, Nakuru and Victoria (Foxall, 1983, Munga, 1985). Residues of organochlorine pesticides have also been reported in several rivers in Kenya (Lalah et al., 2003).

1.6 Hypothesis

Zeolites do enhance the chemical degradation and abstraction of *p, p'* DDT and its degradation products from water sampled from Lake Victoria.

1.7 Justification of the research

Pesticides contaminate water systems through spray drift or run off from agricultural fields where the pesticides find their way into the human system that consumes it. Toxicological effects of pesticides on human include birth defects in children, incontinence and convulsions and fatality amongst others. There is therefore, the need to reduce the quantities of water bound pesticides that eventually are consumed by human being.

Zeolite is viewed as a safe, cheaper, readily available and re-usable method of treating water for both domestic and commercial use as a means of reducing pesticide residues. Although some work has been done on the effect of zeolites on pesticide degradation, there is scanty documented scientific data on the effect of zeolite on the

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degradation kinetics of pesticides, in particular for *p, p'*-DDT. This study is therefore necessary to establish the degradation kinetics of *p, p'*-DDT in the presence of faujasites X and Y zeolites and their efficiency in removal of *p, p'*-DDT and its degradation residues during water treatment. Consequently, the use of zeolites in decontaminating waters of pesticides would be a cheaper, faster and re-usable means of municipal, river and lake water treatments.

The drinking and wastewaters would be free from pesticides residues contamination after shorter treatment duration. The cost of drinking water treatment would decrease leading to a greater access. Secondly, the Kenyan horticulture industries which rely on surface water for irrigation export to other markets especially Europe, which is normally monitored for their pesticide residue levels, may then produce products low in pesticide residual contaminants. Meaning that increased decomposition of water bound pesticides would indirectly lead to increased export volumes for the Kenyan agricultural products.

Generally there is no data on the degradation kinetics of Dichloro – Diphenyl – Trichloroethane (p, p'-DDT) in the presence of Faujasites and zeolite and even in the previous work already done, comparison between X and Y zeolites in their ability on degradation is lacking. This research project was established to explore the use of zeolite as a cheaper and reusable drinking water cleaning agent capable of enhancing pesticide decomposition and removing pesticide residues in drinking waters.

The knowledge of zeolite in purification of organochrorine pesticides is non-existent. This is because virtually no work on their ability in degradation of *p, p'*-DDT has

been done before. It has been established that *p, p'*-DDT, a documented source of pesticides get its way into the Winam gulf in thousands of litres per year (Madadi, 1995). This study was undertaken to establish the rate of degradation of *p, p'*-DDT in Lake Victoria water treated with zeolites. This analysis was meant to bridge the knowledge gap created by lack of documented information on half-lives, quantities of *p, p'*-DDT, *p, p'*-DDD and *p, p'*-DDE in water treated with zeolite.

1.8 Objectives of the study

1. To evaluate if zeolite can remove DDT from water
2. To find out differences between zeolite X and zeolite Y in removal of DDT
3. To identify degradation products of DDT in zeolite X and Y environment
4. To propose the mechanistic pathways of *p, p'*-DDT degradation in the presence of X and Y zeolites.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 General background and study area

The republic of Kenya lies on the eastern side of the continent of Africa, between latitudes 50°40'N and 4°4'S, and Longitudes 33°50'W and 41°45'E. Agricultural production forms the back-borne of Kenya's economy. This sector together with forestry and fishing contributed 28.8 percent of the country's Gross Domestic Product (GDP) in 1997. Agricultural activities are concentrated in the highlands which have high potential and in the Savannah and Coastal which have medium potential AEZs (Kituyi *et. al.,* 1997). The major agricultural products include tea, coffee, horticultural products, pyrethrum, pineapples, sisal, tobacco, cotton, maize, beans, cane sugar, wheat, rice and livestock. The fish resources from the fresh water lakes and the marine water contribute to the fast growing fish industry. To fully realize the economic management of the agricultural production, Kenya heavily depends on the use of the chemical pesticides to control the myriad of insect pests, weeds, and disease pathogens that emerge due to the hot and humid tropical environmental conditions. One of the greatest challenges facing the country is to develop satisfactory techniques that can combine optimal production with good environmental protection practices. Several chemical contaminants from the agricultural fields, comprising pesticides and other agrochemicals have been reported in the drainage systems and are likely to compromise the quality of the water bodies that support the fish industry and domestic human consumption.

The major contaminants commonly detected in the aquatic environment include some organochlorine pesticides used in the agricultural fields, and in the area of public

health vector control. The country's drainage system network and improper handling of these chemicals are likely to be the main contributing factors to their prevalence in the water bodies. The country's principal drainage system begins in the Kenya highlands region. Streams and rivers radiate from the highlands eastwards toward the Indian Ocean, westward to the Lake Victoria, and run northwards to the Lake Turkana or disappear in the arid terrain of Northern Kenya. The seasonal rivers in the Southern highlands of Ethiopia form secondary drainage system, which extend into Kenya along the eastern part of their common boundary. Several smaller rivers begin in the foothills of the Eastern Kenya Highlands in the Tana River basin. Some of these rivers discharge into Lake Victoria and the Indian Ocean Coast of Kenya thus bring pollution loads into these water bodies.

The use of pesticides has certainly increased agricultural production and improved longevity and quality of human life. Coupled with these successes, have been a number of several side effects. Previous research works conducted on the environmental samples including sediments, micro-invertebrate organisms from both marine and fresh water ecosystems have continually revealed contamination by pesticides (Getenga et.,al., 2004b; Wandiga et., al 2002; Barasa 1999; Everaarts et.al.,1997.,Mugachia et.,al.,1992b; Munga 1985). The level of pesticide contamination at the top of the food chain have been exhibited by the presence of residues in cow and human milk and bird eggs (Kanja, 1988;Wandiga and Mutere, 1988;Kahunyo;et., al.,1986). However pesticides are highly toxic compounds and can be very dangerous when mishandled. Fish kills, reproductive failure in birds and acute illness in human have all been attributed to exposure to or ingestion of pesticides as a result of misapplication or careless disposal of unused pesticides and their containers (Rao and Honsby, 1989).Various studies have been conducted to establish links

between pesticides and various carcinogenic, mutagenic tetratogenic, acute toxicity, organ effect, reproductive effects and chronic effects. Pesticide use is still indispensable in Kenya in the areas of agricultural production and public health vector control. However, the toxicity of these compounds and their presence in the environment poses grave issues that oblige the development of methods that will increase agricultural productivity and disease vector control with minimal environmental contamination and side effects to none target species.

Current water purification methods do not completely eliminate pesticides and pesticide residues from domestic water sources. However, use of zeolite is viewed as a possible way of enhancing degradation of pesticides. Due to their nature, the zeolites may not only degrade the pesticides, they may also trap the pesticide molecules by binding (Yang et al., 2006) and hence, concomitantly, eliminate these molecules from the water environment.

2.2 Pesticides

Pesticide are substances or mixture of substances intended for preventing, destroying, repelling, or mitigating the effects of any pest such as insects, mice, animals, weeds, fungi, bacteria and viruses. Though often referred only to include insecticides, the term pesticide also applies to herbicides, fungicides, and other chemical substances used to control pests. Under United States law, a pesticide is also any substance or mixture of substances intended for use as a plant growth regulator, defoliant, or desiccant. Pesticides come in a variety of formulations, to take care of factors such as the nature of the target species, the persistence desired and ease of application (Baker *et al.,* 1988, Berger *et. al.*, 1993)

2.3 Pesticide usage

The use of pesticides in agriculture is a worldwide practice and can be considered beneficial as it serves not only to raise productivity but also to reduce post harvest losses (Gonzales, 1988). In the tropics, pesticides play a vital role in controlling insect vectors of endemic diseases (Getenga, 1999.); however the use of these chemicals has adverse effects on the environment and the health of the people. The major problems challenging the continued use of pesticides are the rising cost of pesticides, pesticides resistance in pest population, insects' pest resurgence and the pesticides residues in the environment (Getenga, 1999). The much publicized use of 1,1 –(2,2,2 – dichloroethylidene) bis (4 – chlorobenzene) (*p, p'*-DDT) by World Health Organization (WHO) for the eradication of malaria is now restricted or banned due to its persistence and bioaccumulation in the fatty tissues of human body (McEwen et al., 1979). Worldwide, it is estimated that there are between 10,000 and 20,000 physically – pesticide diagnosed illnesses and injuries among agricultural workers per year, in developing countries relative to the amount of pesticides used (Vorley *et al.*, 1998). The level of awareness of the dangers posed by the pesticides to the users is low in developing countries, unlike in the developed countries where most, if not all pesticides originate. Pesticides are either categorized as organophosphate (OP) or organochlorine (OC).

Organophosphorous (OP) compounds first appeared in the market in 1945 as the first result of success of the German industry in finding modification of the chemical warfare agents used for insect control; the first to appear were Tepp and O, O – diethyl O, O –dimethyl S (1,2 – dicarbethoxyethyl) phosphorothioate (parathion) followed by O, O – dimethyl S (1,2 – parathion) then O, O – dimethyl S (1,2 –

dicarbethoxyethyl) phosphorothioate (malathion) and many others, four years later (Bey-Dyke et al., 1970, Brown, 1978).

Most organophosphorous insecticides have the structure $(R\text{-}O)_2 - P$ (S or O) X. The two R groups are either ethyl or methyl and are the same in any one molecule while X is frequently a more complex aliphatic, homocyclic or heterocyclic group (Hassal, 1993). In recent years organophosphorous pesticides are replacing many organochloride (OC) pesticides since the former class of compounds were found to be more susceptible to environmental degradation. Organochloride pesticides are more lipophilic and are considered to be more persistent and bioaccumulative at various trophic levels in the food web while organophosphorous compounds are generally short lived and are less bioaccumulative (Minfuse, 1976). For example *p,p'*-DDT; 1,2,3,4,10,10 –hexachloro – 1,4a, 5,8,8a hexahydro – exo -1, 4 endo – 5, 8 – dimethanonaphthalene (Aldrin) and 1,4,5,6,7,8,8, - heptachloro – 3a, 4,7,7a tetrahydro – 4,7 – methano – 1H – Indene (Heptachlor), which are stable, have been banned by United States Environmental Protection Agency (EPA). They have also been banned in Kenya to ratify the UN convention and have all been replaced by organophosphorous compounds (Getenga, 1999). The use of these insecticides inevitably leaves behind residues in the water bodies like rivers, lakes and oceans, which are the main sources of domestic and industrial water supply (Foxall, 1983; Munga, 1985).

2.3.1 Pesticide usage in Kenya

Dichloro-Diphenyl-Trichloroethane (*p, p'*-DDT) has been banned in Kenya since 1997 and has been replaced by organophosphates (Getenga, 1999). Among the

organophosphates that are used are Malathion and Dimethoate, which are used in food crops, horticultural crops and cash crops protection. Malathion is also used as a grain protectant (Acland, 1980). The persistence and fate of these pesticides on the applied targets and non targets depends on such factors as temperature, humidity, light intensity, pH of the media, soil type, organic matter, micro-organism, micro flora and fauna prevailing in the given environment (Gunther *et al.,* 1981). It is known that pesticides are never target specific and as such, aerial application of pesticides must be regarded as potentially hazardous to man and environment. In order to reduce the environmental risks associated with pesticide use, a clear understanding of their degradation rates in specific environment is one of the most important requirements (Getenga, 1999). Extensive studies on the fate of some organochlorines in the Kenyan environmental conditions have been carried out (Wandiga, 1988; Lalah, 1994), and half-life values for *p, p'*-DDT have been found to be 145 days in Nairobi soil under field conditions. Half-life values for *p,p'*-DDT in the water environment have been reported as 56 days in Lake Water and 28 days in river water in the United State(United States Environmental Protection Agency, 1989).

2.3.2 Zeolite application in degrading of pesticides

Research done in Belgrade-Montenegro has reported that the presence of some zeolites in the wastewater enhances the decomposition of pesticide contaminants. Dr Patterson et al., found that zeolites degrade Malathion faster. However, the extent and exact kinetics of such zeolitic action are not yet reported. Zeolites both X and Y types 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 showed that organo-zeolites help remove atrazines,

lindane and diazinon from waters (Jonan et al., 2006). However, application and comparison studies between zeolites-X (low Si/Al ratio) and zeolite-Y (high Si/Al ratio) together with the determination of the rates and order of such pesticide degradation reactions in the presence of zeolites is not yet reported.

2.4 Domestic water sources in Kisumu.

Lake Victoria is the dominant water source in Kisumu municipality and its environs. Water from the lake is treated and distributed for consumption by Kisumu Water Sewerage Company (KIWASCO). The treated and piped water serves a number of estates in the town. River Nyamasaria is yet another source of domestic water. At its old stage, there is a private treatment plant that sells water to the community around. Where piped water is non-existent boreholes have been dug to provide water. In such areas, harvested rainwater is also highly valued. By virtue that only a few estates have piped water, water vending is a common phenomenon in the town. The affluent community within the town relies on bottled water for drinking. The big bottled drinking water is sold in the leading supermarkets in town.

2.4.1 Domestic water treatment.

The domestic water treatment, which is based on the principle of biological decomposition of non-toxic organic wastes using bacteria, goes aerobically as in Scheme 1.

Organic wastes

$$\{C, H, O, F, S\} + O_{2(g)} \xrightarrow{\text{aerobic}} CO_{2(g)} + H_2O_{(l)} + H_2SO_{4(aq)} + NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$$

Scheme.1

After short treatment duration, the liquid effluent remains with much lower organic matter and microorganism. Then chlorinating is done to kill pathogenic microorganisms. The secondary effluent is then treated with Ca $(OH)_2$ to eliminate phosphate as $Ca_5(PO_4)_3(OH)$ at high pH (ca. 11) while NH^+_4 is simultaneously converted to gaseous NH_3. The remaining organic materials are removed through adsorption on activated charcoal and finally nitrogen removed through the action of a combination of nitrifying and denitrifying bacteria (Anil, 1993).

2.4.2 Industrial waste water treatment

Toxic and non-biodegradable chemicals in industrial waste effluent can be purified by filtration using activated charcoal, synthetic resin and membrane techniques.

Activated charcoal adsorbs organic molecules and typical results of which are illustrated in the Table 2 below;

Table 2: Removal of toxic chlorinated organic pesticides (source; Anil, 1993)

Compound	Initial Concentration (µg/l)	Concentration after Activated charcoal treatment	Organic reduction (%)
Aldrin	48	< 1.0	99 +
Dieldrin	19	0.05	99 +
Endrin	62	0.05	99 +
DDT	41	0.1	99 +
Arochlor 1242 (PCB)	45	<05	99 +

2.4.3 Drinking Water Treatment and limitations.

Water treatment plants work in three steps, which include aeration to settle suspended matter, coagulation of small particles and suspended matter by lump and ferric chloride and finally disinfecting by chlorinating to kill germs and bacteria. But chlorinating has been discovered to give rise to $CHCl_2$ and other chlorinated organics,

which are toxic to humans (Anil, 1993). Environmental Protection Agency has fixed permissible dose of $CHCl_2$ at 100 ppb, which is achieved by subjecting chlorinated water to activated carbon. Also, ozonation can be used but it is expensive due to energy consumption and its chemical instability as it decomposes into O_2 (Anil, 1993).

In domestic and drinking water treatments, pesticides and pesticide residues are hardly removed. In industrial wastewater treatment activated charcoal removes toxic chlorinated organic but however, *p, p'*-DDT, *p, p'*-DDE and *p, p'*-DDD remain un-removed. More so activated charcoal is expensive and in most cases un-reusable (Anil, 1993).

CHAPTER THREE

3.0 METHODOLOGY

3.1 Study site

This study was designed to investigate the fate and degradation kinetics of *p, p'*-DDT in the Lake Victoria water in the presence of zeolites. Lake Victoria is the largest of all the African lakes, and the second widest fresh water body in the world. It has a shoreline of 3,440 km long, and catchment area of 184,000 km^2. The main land uses of the Kenya side of Lake Victoria catchment area range from natural landscape to agriculture. The primary industries in the water catchment's area comprises of cash crops such as coffee, tea, cotton, sugarcane, animal husbandry and fisheries. Secondary industries consist of coffee and tea processing, sugar, palm, dairy products, foods, leather and textile. The Lake is mainly used as source of water for industrial and domestic purposes, navigation and transportation, recreation (yatching), and fisheries. The major concern about the current state of the Lake's environment centers on the accumulation of the agricultural and industrial chemicals that are washed into the rivers during rainy season and end up in the Lake. These chemicals are toxic and pose a threat to the aquatic organisms and man. (Getenga *et al.*, 2004b).

3.2 Chemicals used

Pesticide chemical standards of *p, p'*-DDT, *pp*-DDE and *p, p'*-DDD used for purging, identification and quantification in the field's samples were more than 99% and were donated by Prof. Wandiga of University of Nairobi (UoN). White spot Nitrogen gas used for Gas Chromatogram (GC) equipped with Electron Capture Detector (ECD) was supplied by BOC Kenya LTD. Florisil (magnesium silicate 60-100 mesh) used for cleaning samples was of high purity (over 99%) and was supplied by Kobian

Kenya LTD. Analytical grade n-hexane, acetone, iso-octane and anhydrous sodium anhydrous sulphate were supplied by Zeta Chemicals Kenya LTD. Faujasite –X and Y Zeolite were obtained from Sigma and Aldrich.

3.3 Equipment and apparatus used

Degradation experiments were carried out in un-corked 1.8 litre glass jars. Analytical balance type A-160 from Fischer scientific was used for all weight measurements, whereas a Gallenkamp oven model OV-160 was used for drying of all the glassware before use. A 100ml glass separating funnel was used in solvent-solvent extraction of water samples. Glass columns of length 60 cm and 2 cm internal diameter were used in the clean up procedures, LABCONCO rotary evaporator was used for concentrating the sample extracts. A laboratory line explosion proof refrigerator kept at a temperature of -15^{o}C was used for temporary storage of the field samples before analysis and REVCO deep freezer was used for storage of degradation samples after extraction. Varian chromapack CP-3800 and 3400 gas chromatographs equipped with, ECD detector was used for analysis of the *p, p'*-DDD, *p, p'*-DDT and *p, p'*-DDE in the samples.

3.4 Experimental setup

Experiments were carried out in a green house at Maseno University-Kenya between the months of October 2006 and April 2007, where tropical conditions were at play. In the sample containers were;

1. 1 litre of water + 0.3 g zeolite (separately X and Y zeolites)
2. 1 litre of water + varied amount of pesticide + 0.3 g zeolite (X and Y)

3. 1 litre of water (control 1)
4. 1 litre of water + pesticide (control 2)

All the treatments were in triplicates and the three concentrations of *p, p'*-DDT used were; 5 ppm, 10 ppm and 20 ppm respectively. The weighed crystals of pesticides were first dissolved in 3 mls of triple distilled acetone before purging in the experimental waters.

The water samples were collected, extracted, cleaned and analyzed for either *p, p'*-DDD, *p, p'*-DDE or *p, p'*-DDT. Identification and quantification of the *p, p'*-DDT and its residues then followed.

The physico-chemical properties of water used for this study were determined at Maseno University laboratory.

3.5 Experimental procedure

The degradation experiments were carried out using filtered Lake Victoria water treated with 0.3 g of zeolite per litre of water. The 5 µg, 10 µg and 20 µg of *p,p'*-DDT were dissolved in 3 mls of acetone and then diluted to Lake water to give a concentration of 5 µg/l, 10 µg/l and 20 µg/l respectively in the separate jars containing 0.3 g of zeolites X and Y separately. The solutions were stirred periodically with a glass rod to distribute the pesticide residues evenly throughout the water during sampling intervals.

3.6 water Sampling

After stirring, the water was sampled from the 1.8 litre glass containers by grab method into 40 ml amber bottles, which had been pre-washed with distilled water and dried. The samples were kept in icebox containing wet ice during sampling trip.

3.6.1 Field sampling and extraction procedure

The lake water used was collected from Kaloka beach at the shores of Lake Victoria into acid washed plastic containers and stored at room temperature in the dark for two weeks before using it in the experiments. Sampling of water from greenhouse was carried out at specific times after the initial zeolite treatment of water i.e. after 2 hrs, 5 hrs, 8 hrs, 22 hrs, 48 hrs, 120 hrs, 240 hrs, 720 hrs, respectively and kept in a refrigerator at 4 ^{O}C after sampling trip, prior to extraction.

3.6.2 Extraction of water samples

The water samples were extracted by solvent-solvent extraction method. 40 ml of water was transferred into 1.0 litre separatory funnel, and then 20 ml triple distilled n-hexane was added and shaken for 5 minutes, while releasing pressure, and allowed to settle for 30 minutes for better separation of phases. The upper organic layer was collected into clean-dry 100 ml conical flask and kept at 4^{0}C in a refrigerator. The extraction was repeated twice, using 20 ml portions of n-hexane. The extracts were combined and concentrated to 10 ml using LABCONCO rotary evaporator prior to clean up.

3.6.3 Clean up of the water extracts

The concentrated pesticide extracts were purified from extractants by passing through 60 cm long X2 cm column packed with 10 g of florisil (magnesium silicate, 60-100 mesh) and topped with 2 g anhydrous sodium sulphate. The pigments were removed by adding 0.5 g of activated charcoal on top of sodium sulphate. Pesticide residues were sequentially eluted with 100 ml of isooctane. The eluates were concentrated to near dryness using a rotary evaporator at 70^0C and reconstituted in 100 µl of isooctane for Gas Chromatography (GC) analysis.

3.7 pH determination for the water samples

The pH values of water samples were determined using accument model 15- Fischer scientific pH meter. Before any reading was taken, the pH meter was calibrated using buffer solutions of pH 4, 7 and 10. The pH was determined directly by having 50 mls of the water in the beaker and immersing the pH meter into the water. All pH readings were recorded at room temperature (approximately 24^0C).

3.8 Recovery studies

Recovery of pesticide residues from the deionised water was done to determine the extraction efficiencies of the methods used. This was achieved by spiking the standard samples of *p, p'*-DDT pesticides and its metabolites; *p, p'*-DDE and *p, p'*-DDD into deionised water then allowed to stay for 15 minutes and extracted using the same procedures as for the field samples in section 3.6.2. Cleaned extracts were injected into GC-ECD the chromatograms were used to determine extraction efficiencies.

3.9 Gravimetric determination of chloride ions

Gravimetric analysis of chloride ions was based on the quantative isolation through precipitation as silver chloride solid by using silver nitrate solution. The 30 ml analytes were in 100 ml conical flasks (faujasite X and faujasite Y treated), which were heated on a hot plate to keep them warm. Stirring was done with a glass rod as $AgNO_3$ solution was added in excess to precipitate the Cl^- ions and then left for one hour to digest. Filtration was done to separate the supernatant liquid. The precipitate was dried in the oven at 140^{O}C for two hours cooled in a decicator and then weighed. From the weights of the precipitates and that of the sample, the percentage of the constituent in the original sample was calculated.

3.10 Cleaning of glassware and other items

The glassware were soaked in chromic acid for at least 4 hrs, washed with tap water then followed with distilled water and finally rinsed with triple distilled acetone. Drying of the glassware was done in a Gallenkamp oven at 105^{O}C for 4 hrs. Florisil and anhydrous sodium sulphate were activated at 350^{O}C and 200^{O}C respectively before they were used in the clean up process (UNESCO, 1993).

3.11 GC analysis of extracts

Analyses of *p, p'*-DDT pesticide residues were carried out using the Varian Chrompack CP-3800 GC. The GC was equipped with Ni^{63} ECD and CP-SIL 8CB-15 m, 0.25 mm (i.d), and 0.25 mm film. The Column temperature was programmed at 150^{O}C (1 min), changed at 4^{O}C/min to 200^{O}C (0 min), and 4.5^{O}C/ min to 300^{O}C. Injector temperature was maintained at 250^{O}C, and at 300^{O}C for the detector, and a flow pressure of 30 Psi of Nitrogen gas was applied for the carrier gas. Sample size of

1 µl and split ratio of 1:20 was used for all the samples. Data processing was done using Star Version 5.4. Sample analysis was carried out by injecting 1 µl sample size into the GC column, identification and quantification was accomplished by external standards method.

3.12 GC-MS analysis of extracts

GC-MS analysis of the external standard mix was done to verify if the compounds detected in the GC-ECD analysis were the actual target compounds. The GC-MS conditions used were as specified below:

Carrier gas	Helium
Column	DB-5,60 M,ID-0.25
Injector temperature	320^{O}C
Initial oven temperature	110^{O}C
Final temperature	320^{O}C
Injection volume	2.0µ

3.13 Infrared measurements

A mixture of ca. 1% sample and ca. 99% IR grade KBr (to dilute the sample for better resolution) was ground in a glass mortar to fineness. Then ca. 0.10 gram of the ground mixture was pressed at 10 Ton pressure for ca.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 – 400 cm^{-1} range. The FTIR spectrometer was calibrated by checking the deviation between the literature and experimental polystyrene spectral band positions. The root mean square deviation (RMSD) for the two spectra was 1.32 cm^{-1}.

3.14 X-ray diffraction measurements

The X-ray diffraction data was collected at room temperature on a Scintag XDS 2000 powder diffractometer using Cu kα radiation of λ = 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 $5^{\circ} \leq 2\theta \leq 45^{\circ}$.

3.15 Determination of rate and half life of reaction

a hypothetical reaction thus

$$A \longrightarrow B \quad \text{----------[1]}$$

Where

A = Reactants.

B = Products.

The general rate law can be written as

$$-\frac{d[A]}{dt} = K[A]^n \quad \text{----------[2]}$$

Where

[A] = Concentration of species A.

dt = Change in time.

K = Rate constant.

When n ≠ 1, then integration of this equation gives;

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)Kdt \text{ ---------- [3]}$$

n – Can either be a fraction or an integer.

For Zeroth Order, n=0 then;

$$\frac{-dA}{dt} = K[A]^0 = K \text{ ---------- [4]}$$

-dA = Kdt

$$\int_{[A]_0}^{[A]} d[A] = K\int_0^t dt$$

$$[A] = [A] - Kt \text{ ..... [5]}$$

For half life $\left(t\,1/2\right)$

$$\frac{[A]_0}{2} = [A]_0 - Kt\,1/2$$

$$t\,1/2 = \frac{[A]_0}{2K} \text{ ..... [6]}$$

For first Order, n=1 then;
Then rate law can be written as

$$Rate = K[A]^1 = \frac{-d[A]}{dt}$$

and thus

$$\frac{-d[A]}{dt} = Kdt \text{ .....[8]}$$

Where

[A] = Concentration of species A.

dt = Change in time.

K = Rate constant.

When integrated between limits of time = 0 and time =(t) later time

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$$\int_{[A]}^{[A]_o} \frac{-d[A]}{[A]} = K \int_0^t dt \quad \text{.....[9]}$$

This becomes

$$\ln \frac{[A]_o}{[A]} = Kt + C \quad \text{.....[10]}$$

It can be written as

$\ln[A]_o - \ln[A] = Kt$

$\ln[A] = \ln[A]_o - Kt$ .....[11]

Upon relation to the usual equation of a straight line:

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

From [11]

$[A]_o$ – Initial concentration

$\ln[A] = y$

$-K$ = Gradient

$b = \ln[A]_o$, constant, y intercept

Then a plot of ln[A] against time (t) will give a straight line that satisfies the above condition. That is gradient (-K) = rate constant, y intercept = natural log of initial concentration

Likewise half-life can be derived from equation 11 as,

Let $\lambda = t_{½}$ = half -life

Then

$$\ln \frac{[A]_o}{[A]} = \ln \frac{[A]_o}{\left[\frac{A}{2}\right]} = K\lambda = \ln 2 \quad \text{---------- [12]}$$

Thus

$K\lambda = 0.693$

$\lambda = \frac{0.693}{K}$ .....[13]

For second Order, n=2 then;

Rate = $K[A]^2 = -d\frac{[A]}{dt}$ ---------- [14]

Re-arrange equation

$-\frac{d[A]}{[A]^2} = Kdt$ ---------- [15]

Equation integrated within limits of concentration at t = 0 and [A] at time(t)

$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = K\int_0^t dt$ it gives ---------- [16]

$\frac{[A]_0}{2} - \frac{1}{[A]_0} = Kt \quad t = \frac{1}{K[A]_0}$ ---------- [17]

For third Order, n=3 then;

$-\frac{d[A]}{dt} = K[A]^3$ ---------- [18]

$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2Kdt$ ---------- [19]

$t_{½} = \frac{3}{2K[A_0]^2}$ ---------- [20]

Half-life is the time taken for the initial amount of substance available to reduce to half of its quantity after disappearance.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

The knowledge of zeolite in degradation of organochlorine pesticides is non-existent. This is because virtually no work on their ability in degradation of *p, p'*-DDT has been done before. It has been established that *p, p'*-DDT, a documented source of pesticides (Wandiga et. al, 2004) gets it way into the Winam gulf in thousands of litres per year. This study was undertaken to establish the rate of degradation of *p, p'*-DDT in Lake Victoria water treated with zeolites. This analysis was meant to bridge the knowledge gap created by lack of documented information on half-lives, quantities of *p, p'*-DDT, *p, p'*-DDD and *p, p'*-DDE in water treated with zeolite.

4.1.0 Authentication of results

Based on GC-MS library, the GC-MS identified the target compounds at different retention times as shown in Table 3.

Table 3: The GC-MS retention times (min) for the external standard organochlorine.

Target compound	Retention time (min)
PCB155	20.133
2, 4 *p, p'*-DDT	20.249
4, 4 *p, p'*-DDD	24.929
2, 4 *p, p'*-DDT	25.298
4, 4 *p, p'*-DDT	27.804

The GC-ECD retention times for the same external standard mix are also given in Table 4 below;

Table 4: The GC-ECD retention times for the identified organochlorine (min).

Target compound	Retention time (min)
p, p'-DDT	8.532
p, p'-DDE	5.423
p, p'-DDD	8.013
PCB155	3.654

4.1.1 Recovery of 10 µg/ml *p, p'*-DDT from de-ionized water and Lake Victoria water

Recovery efficiencies of 97.20 ± 0.04 and 98.61 ± 0.02 percent were obtained for *p, p'*-DDT extractable residues in water to be treated with zeolite Y and X as shown in Table 5 below;

Table 5: Recovery efficiencies of extractable residues of 10 µg/ml *p, p'*-DDT in deionised water and lake water to be treated with zeolite

Amount		Extractable residues	
Pesticide/water type	Spiked µg/ml	Amount recovered µg/ml	Recovery rate % recovery
De-ionized water	10.00±0.00	9.82±0.01	97.20±0.04
Lake Victoria water	10.00±0.00	9.86±0.00	97.43±0.01

Mean ± sd; N = 3

Note: De-ionized water was found to have no detectable *p, p'*-DDT residues but lake water was found to have 0.12 ppm of *p, p'*-DDT before spiking.

4.1.2 Degradation of 5 µg/ml *p, p'*-DDT in lake water under different treatments

Enhanced degradation rates were observed from the treated water (dosed with zeolite). The rates were faster in the first 2 minutes than in the untreated water (Table 6). However, water with zeolite treatments, the concentrations went down to Below Detection Limit (BDL) after 5 hours of application. Water without zeolite treatments maintained a concentration of 2.46 µg/ml of the *p, p'*-DDT unchanged as compared to BDL *p, p'*-DDT levels of treated water.

Table 6: Dissipation of 5µg/ml *p, p'*-DDT in lake water under different treatments

Time Hours	X + water µg/ml	Y + water µg/ml	water alone	% removed by X	Y
2	0.66±0.000	1.54± 0.007	4.71± 0.000	85.99	67.30
5	BDL	BDL	4.05± 0.007	100	100
8	BDL	BDL	3.01± 0.071	100	100
22	BDL	BDL	2.51± 0.007	100	100
48	BDL	BDL	2.46± 0.000	100	100
120	BDL	BDL	2.46± 0.071	100	100
240	BDL	BDL	2.46± 0.000	100	100
300	BDL	BDL	2.46± 0.000	100	100

Mean ± sd; N = 3

BDL- Below Detection Limit

4.1.3 Dissipation of 10 µg/ml *p, p'*-DDT in lake water under different treatments

Enhanced degradation rates were observed from the treated water (dosed with zeolite). In water treated with zeolite X and zeolite Y (Table 7), the rates were faster in the first 10 minutes as compared to the untreated water. However, water with zeolite X treatment, the concentration went down to Below Detection Limit after 120 hours of application. Water treated with zeolite Y maintained a concentration of 0.67 µg/ml of the *p, p'*-DDT unchanged as compared to 4.93 µg/ml of untreated water.

Table 7: Dissipation of 10 µg/ml *p, p'*-DDT in lake water under different treatments

Time Hours	X + water	Y + water	water alone	% removed by	
	µg/ml	µg/ml	µg/ml	X	Y
2	4.34± 0.007	3.46± 0.007	9.42±0.000	53.93	63.27
5	1.83± 0.000	3.08±0.071	8.11±0.007	77.44	62.02
8	1.00± 0.000	1.25±0.000	6.02±0.007	83.39	79.24
22	0.47± 0.007	0.81±0.021	5.02±0.071	90.68	83.86
48	0.02± 0.007	0.67±0.007	4.93±0.000	99.60	86.41
120	BDL	0.67±0.007	4.93±0.071	100	86.41
240	BDL	0.67±0.007	4.93±0.000	100	86.41
300	BDL	0.67±0.007	4.93±0.000	100	86.41

Mean ± sd; N = 3

BDL- Below Detection Limit

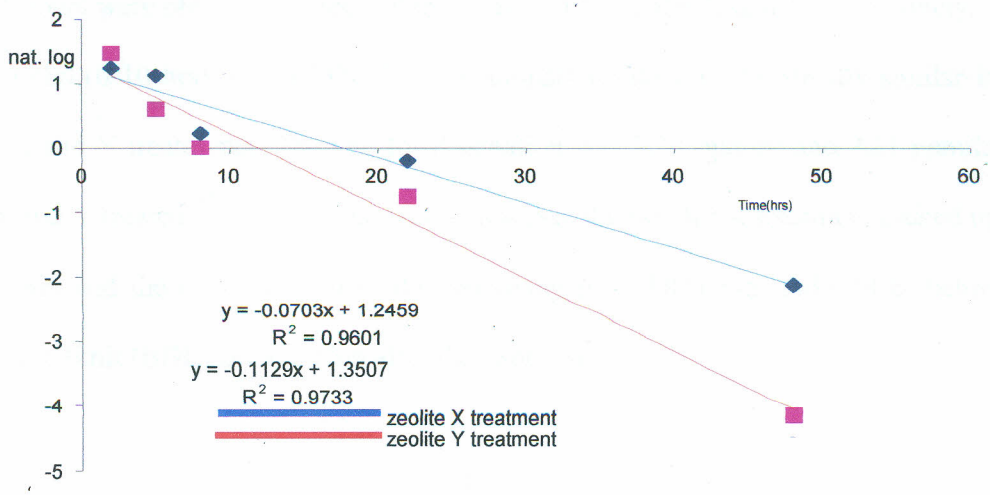
4.1.3.1 Mean loss rate coefficients for 10 µg/ml *p, p'*-DDT in Lake Victoria water under different treatments.

Table 8: Mean degradation rate constant K and R^2 for different orders of reaction under zeolite X treatment.

Order of reaction	R^2	K Value
Zero	0.5171	-0.0648
First	0.9731	-0.1074
Second	0.8598	1.0735
Third	0.8377	53.976

Mean degradation rate constant K, R^2 values and half-lives (see equation 1-5) were calculated from the replicate samples. Using the product-moment correlation coefficient, r or the coefficient of determination R^2 checks linearity. The values are illustrated in the Table 8 as shown above. These values were obtained after fitting data for order 0, 1, 2 and 3 as shown in Figure 5 below for first order rate.

Figure 5: Degradation rate coefficient for water treated with zeolite X to Y



4.1.3.2 Trend of 10 µg/ml *p, p'*-DDT dissipation in Lake Water under different treatments

The amounts of *p, p'*-DDT remaining in the sample waters after specific durations, in hours, are presented in the Figure 6 below.

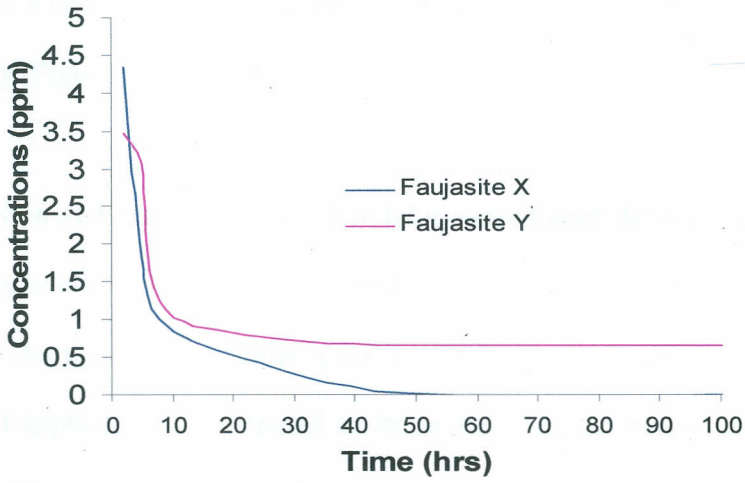


Figure 6: Amount of *p, p'*-DDT remaining in solution with time in both zeolites X and Y treated samples

The data in Figure 6 shows that the concentrations of *p, p'*-DDT in the presence of both X and Y zeolites decreased with time. The rate of the degradation of the *p, p'*-DDT in Lake Victoria water in the presence of both zeolites X and Y was determined to be a pseudo-first order one. The calculated half lives ($t_{1/2}$) of 6.1 ± 0.001 and 14 ± 0.001 hours were obtained for the waters treated with zeolites X and Y, respectively. The initial (0-10 hrs) of *p, p'*-DDT decontamination rate was statistically similar in both X and Y treatments. The rate for dissipation was 3.34 ppm/hr and 2.21 ppm/hr for X and Y treated samples respectively. However the rate for X treatment picked up thereafter and the concentration of the remaining *p, p'*-DDT was reduced to below detection limit (BDL) at ca. 50 hrs after the exposure.

4.1.3.3 Chemo dynamics of 10 µg/ml *p, p'*-DDT dissipation in Lake Victoria water

From Table 8, the first order rate was determined to be the most fitting therefore, the Pseudo-first order kinetic rate equation (equation 6) was used to describe the dissipation of *p, p'*-DDT in Lake Victoria water. The calculated half lives of 6.1±0.001 and 9.6±0.001 hours were obtained from water treated with zeolite X and Y respectively (Figure 5)

4.1.4 Dissipation of 20 µg/ml *p, p'*-DDT in lake water under different treatments

Enhanced degradation rates were observed from the treated water (dosed with zeolite). In water treated with zeolite X and zeolite Y the rates were faster in the first 10 minutes of application as compared to the untreated water. However, water with zeolite X treatment, the concentration went down to 4.93 after 120 hours of application. Water treated with zeolite Y maintained a concentration of 5.60 µg/ml of the *p, p'*-DDT unchanged as compared to 7.02 µg/ml of untreated water as shown in Table 9 below.

Table 9: Dissipation of 20 µg/ml *p, p'*-DDT in lake water under different treatments

	Treatments				
Time Hours	**X + water µg/ml**	**Y+water µg/ml**	**water alone**	**% removed by X**	**Y**
2	13.76±0.007	12.88± 0.007	18.42± 0.000	25.30	30.08
5	9.94± 0.000	11.19± 0.071	16.22± 0.007	38.72	31.1
8	7.02± 0.000	7.27± 0.000	12.04± 0.071	41.69	39.62
22	5.49± 0.007	5.83± 0.021	10.04± 0.007	45.32	41.93
48	4.95± 0.007	5.60± 0.007	9.86± 0.000	43.20	43.20
120	4.93± 0.006	5.60± 0.007	8.11± 0.071	39.21	30.95
240	4.93± 0.007	5.60± 0.007	7.02± 0.000	29.77	20.23
300	4.93± 0.000	5.60± 0.007	7.02± 0.000	29.72	20.23

Mean ± sd; N = 3

4.1.4.1 Trend of 20 µg/ml *p, p'*-DDT dissipation or loss in Lake Water under different

Treatments

The amounts of *p, p'*-DDT remaining in the sample waters after specific durations, in hours, are presented in the Figure 7 below.

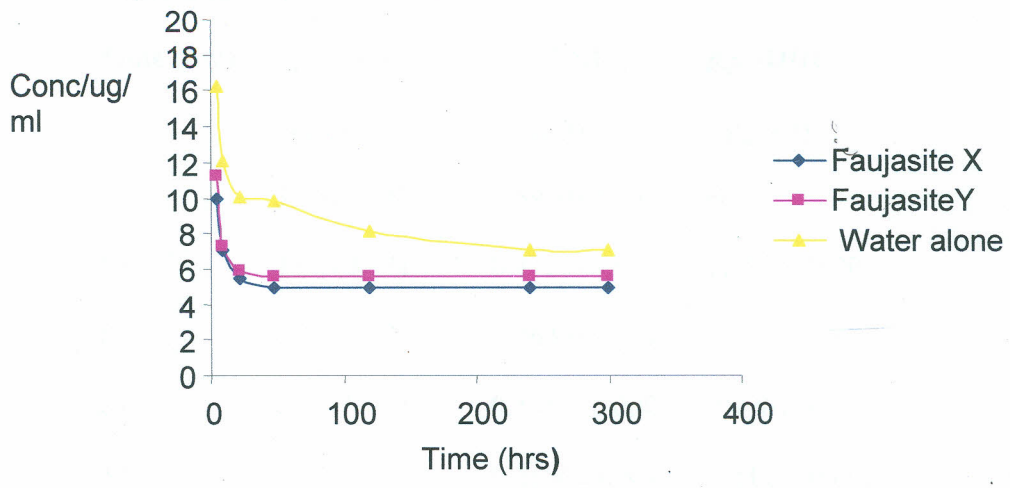


Figure 7: Amount of *p, p'*-DDT remaining in solution with time in both zeolites X and Y treated samples

4.1.5 Distribution of 10 µg/ml *p, p'*-DDT, *p, p'*-DDE and *p, p'*-DDD in treated Lake Victoria water

4.1.5.1 Zeolite Y treatment

There was a considerable decrease in the concentration of *p, p'*-DDT and *p, p'*-DDE in the treatment. Although concentration of *p, p'*-DDD kept on increasing as shown in Table 10 below;

Table 10: Distribution of 10 µg/ml *p, p'*-DDT, *p, p'*-DDE and *p, p'*-DDD in treated lake Victoria water

Time (hrs)	*p,p'*-DDT (µg/ml)	*p,p'*-DDE (µg/ml)	*p,p'*-DDD (µg/ml)
2	3.46±0.007	0.5910±0.006	BDL
5	3.08±0.071	0.4720±0.005	0.0054±0.006
8	1.25±0.000	0.2649±0.001	0.0033±0.007
22	0.81±0.021	0.1610±0.000	0.1961±0.010
48	0.67±0.007	0.2156±0.004	0.3113±0.000
120	0.67±0.007	0.2671±0.000	0.3116±0.000
240	0.67±0.007	0.2654±0.000	0.3112±0.000

Mean ±sd; N=3

During the study, a considerable decrease in the concentration of *p, p'*-DDT remaining in the Zeolite Y treated water samples was observed. This trend is plotted in Figure 8. The concentration of the products (both *p, p'*-DDE and *p, p'*-DDD) also generally increased with time.

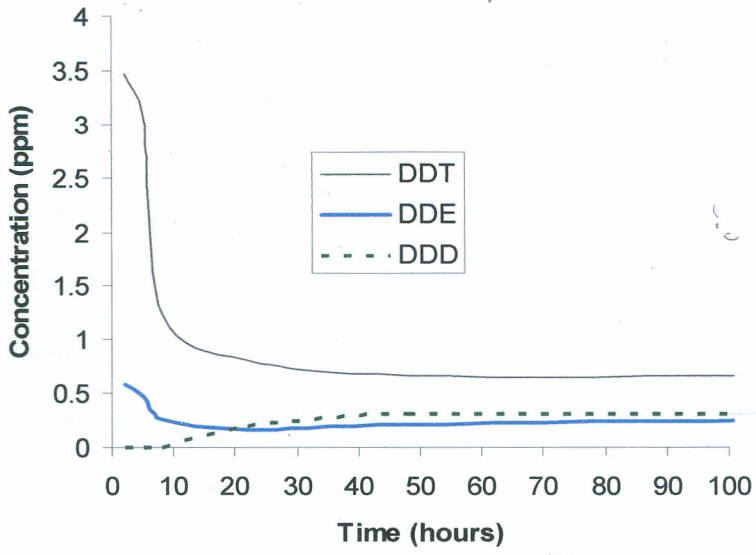


Figure 8: The concentration of the *p, p'*-DDT and its degradation product with time in Zeolite Y.

After the 5th hour of exposure, both *p, p'*-DDD and *p, p'*-DDE could be detected. Specifically, the *p, p'*-DDE concentration, which was initially higher than that of *p, p'*- DDD, reduced in magnitude and in ca. 18 hrs, was overtaken by the *p, p'*-DDD. At the same time, the concentration of *p, p'*-DDD kept on increasing for the duration of the study even though this concentration remained lower as compared to that of remnant *p, p'*-DDT (Figure 8).

From the Figure 10, out of the initial *p, p'*-DDT concentration of 10 ppm, only concentration of 3.46ppm was water bound at the end of the first 2 hours, meaning that some 6.53 ppm of *p,p'*-DDT had been either degraded or just adsorbed into the zeolite. In addition, the glass containers were only found to retain ca. 0.01 ppm of the applied 10 ppm *p, p'*-DDT. In our control set-up, other loses such as through evaporation to surrounding air, photodecomposition, volatilization (Wandiga et al., 1996) were taken care of. Thus only entrappement within the Faujasite Y cages (Yang

et. al, 2006) and degradation remain as the possible means of reducing the concentration of *p, p'*- DDT in the water solution.

4.1.5.2 Zeolite X treatment

The *p, p'*-DDT concentration declined up to BDL after 48 hours (Table 11). The only detectable breakdown product was *p, p'*-DDE, whose concentration peaked at 5 hours after exposure and then declined with time to BDL at around 20 hours.

Table11: Distribution of 10 µg/ml *p, p'*-DDT, *p, p'*-DDE and *p, p'*-DDD in treated Lake Victoria water

Time (hrs)	*p,p'*-DDT (µg/ml)	*p,p'*-DDE (µg/ml)
2	4.34±0.001	0.0055±0.000
5	1.83±0.002	0.1203±0.000
8	1.00±0.001	0.1118±0.000
22	0.47±0.000	BDL
48	0.02±0.001	BDL
120	BDL	BDL
240	BDL	BDL

Mean ±sd; N=3

The concentration of *p, p'*-DDT decreased to BDL after ca. 48 hours (Table 11) of contact time. During which time, the only detectable breakdown product was

p, p'-DDE. In both Zeolite Y (Figure 8) and X (Figure9), the concentration of the product *p, p'*-DDE peaked after 5 hours.

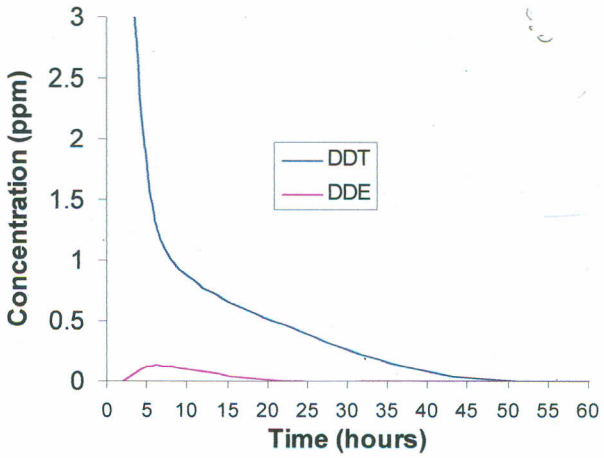


Figure 9: The concentration of the *p, p'*-DDT and its degradation products in X zeolites environment

Unlike in Y treated samples where the *p, p'*-DDE could be detected for longer durations of the study, in X treatments, the decline in concentration was sharper. The concentration of *p, p'*-DDE (Figure 9) went to below detection limit in just 20 hours after exposure.

The concentration of the only breakdown product (*p, p'*-DDE) increased from the 2nd hour up to the 5th hour and then dropped to BDL in 20 hrs (Table 11)

4.1.6. The infra red (IR) spectra of the ring vibration of Faujasite Y at 10ppm DDT level

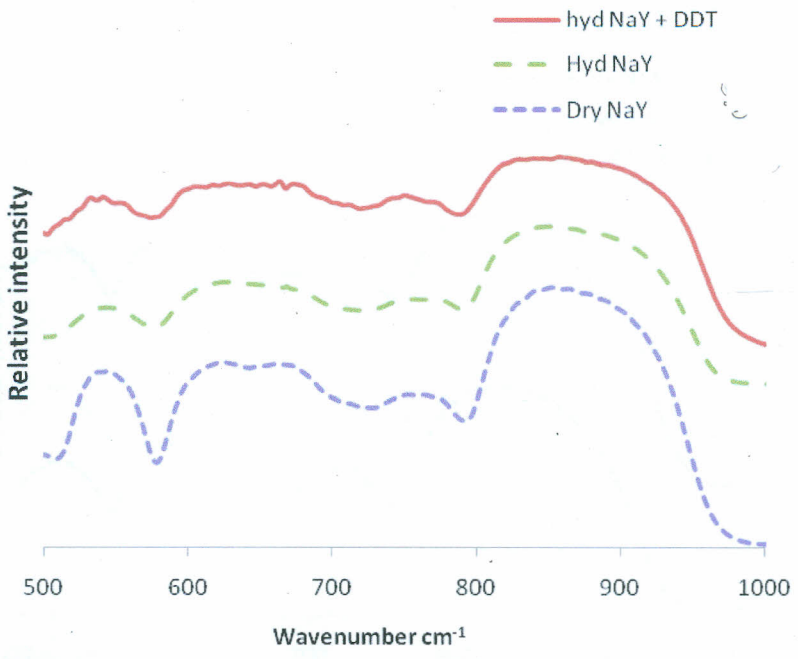


Figure 10: The IR spectra of the ring vibration region of Faujasite Y. where bottom spectrum is for activated dry NaY, middle one hydrated NaY, and upper most for hydrated NaY exposed to 10 ppm DDT.

From the IR Fig. 10, the most distinct changes upon the exposure of the hydrated NaY to the 10 ppm DDT was the shifting of the Single four ring (S4R – site III) (see Fig. 4) symmetric stretching mode from ca. 796 cm^{-1} for both spectrum [a] and [b] to ca. 785 cm^{-1} for DDT exposed NaY in spectrum [c] (Kowenje *et, al.*2010; Lui *et, al.*1995). The other rings at ca. 750 and 580 cm^{-1} for Single Six ring (S6R – Site II) and Double six ring (D6R – Site I) were least affected by the exposure of the hydrated NaY to DDT.

4.1.7. The infra red spectra of the ring vibration of Faujasite X at 10ppm DDT level

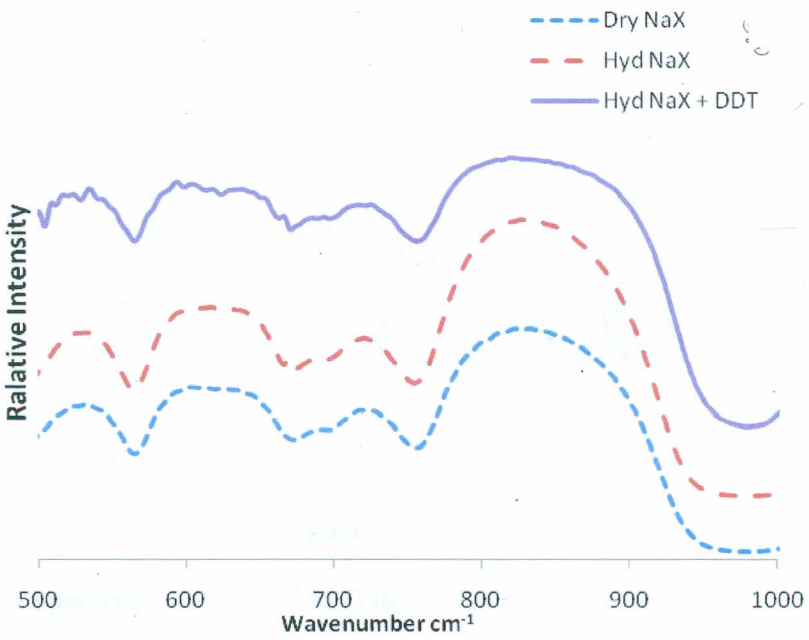


Figure 11: The IR spectra of the rings vibration region of Faujasite X. Where bottom spectrum is for activated dry NaX, middle one for hydrated NaX, and the upper most is for Hydrated NaX exposed to 10 ppm DDT.

From the IR Fig. 11, the most distinct changes upon the exposure of the hydrated NaX to the 10-ppm DDT were the shifting of both S4R and S6R vibration modes. The Single four ring (S4R) symmetric stretching mode shifted from ca. 796 cm-1 for both spectrum [a] and [b] to ca. 785 cm^{-1} for DDT exposed NaX in spectrum [c] while the S6R subtly moved from ca. 680 cm^{-1} for activated and hydrated NaX to ca. 670 cm-1 upon exposure to 10 ppm of DDT (Kowenje *et, al.*2010; Lui *et, al.*1995). The Double six ring (D6R) was least affected by the exposure of the hydrated NaX to DDT.

4.1.8. The X-ray diffraction of Faujasite Y at 10 ppm DDT level

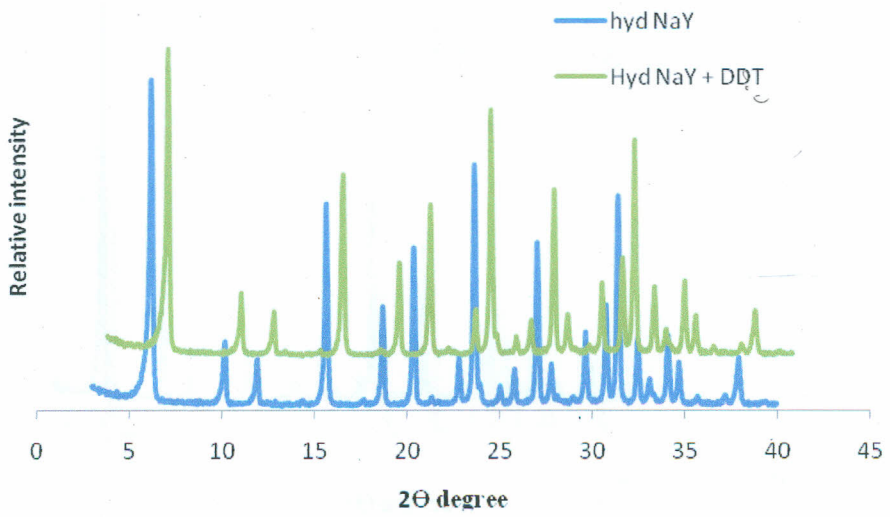


Figure 12. The XRD of the hydrated NaY and hydrated NaY + 10 ppm DDT. The upper spectrum is shifted 0.02□ degree to the right.

In the Fig. 12, the peaks are more intense and sharper for the hydrated NaY than for hydrated NaY + DDT. Specifically, for the sample exposed to DDT, a subtle reduction of ca. 5% in the relative intensity of the peak 11.9 2θ (*311 - indices*) compared to that of 10.12 2θ (*220 - indices*) (Kowenje *et, al.*2010; Salama *et, al.*2006) belonging to hyd NaY was recorded.

4.1.9. The X ray diffraction of Faujasite X at 10 ppm DDT level

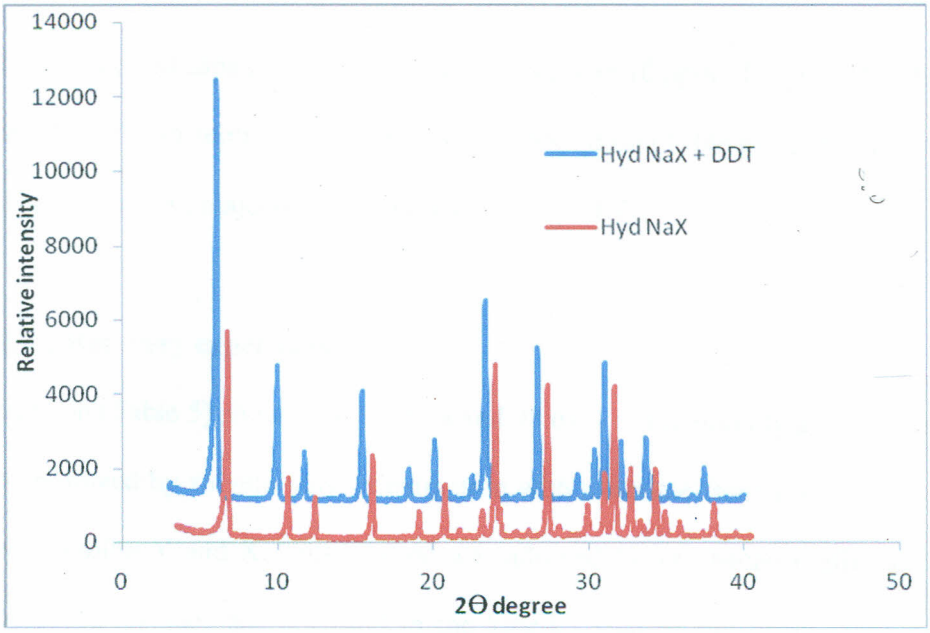


Figure 13. The XRD of the hydrated NaX and hydrated NaX + 10 ppm DDT. The upper spectrum is shifted 0.02□ degrees to the right.

In the Fig. 13, the peaks are more intense and shaper for the hydrated NaX than for hyd NaX + DDT. Here the DDT exposed sample, unlike in NaY case, registered a significant reduction of ca. 45% in the relative intensity of the peak 11.9 2θ (*311 - indices*) compared to that of 10.12 2θ (*220 - indices*) belonging to Hyd NaX.

4.2 DISCUSSION

Due to limited capacity of water to hold more than 10 ppm of *p, p'*-DDT (Table 9) and also due to zeolites absorbing all the 5 ppm dose (Table 6), subsequent discussions will majorly be for the 10 ppm *p, p'*-DDT dosing level.

4.2.1 Recovery experiment

Data on (Table 5) shows that 97.20% and 98.61% of the initially applied pesticide can be removed by solvent-solvent extraction with n-hexane from water before treatment with zeolite Y and X. This method was adopted for use because after all the bound pesticide residues are not used in the kinetics studies and again these percentages compare well with values quoted in the literature (Wandiga et. al, 2004; Wandiga et. al, 1996).

4.2.2 Dissipation trend of *p, p'*-DDT from treated Lake Victoria water

Capacity of both zeolites (X and Y) exceeded the 5-ppm dose. The initial fast rate of dissipation of the extractable residue up to the 8^{th} hour (both X and Y) is due to the high initial concentration of

p, p'-DDT on the water surface (Figure 7). With time, the rates of these processes are reduced as the concentration of the extractable form is reduced. In the second phase, the dissipation rate is low which is attributed to reduced concentration of the extractable form of *p, p'*-DDT residues (Figure 7). The loss is again attributed to catalytic decomposition and adsorption by the zeolite matrix (Yang et. al, 2006; Kanyi *et.al*, 2006). From Table 7, the concentration of undecomposed *p, p'*-DDT after a period of 48 hours was constant at 0.67 ppm for Y zeolite treatment up to the end of the experiment (240 hours) but that of X went to below detection limit (BDL) after

120 hours (Table 7). This could be due to the more catalytic and adssorptive nature of zeolite X as compared to that of Y as noted by Kowenje et. al 2006.

4.2.2.1 Fate of *p, p'*-DDT in Lake Victoria water treated with Faujasite Y Zeolite

There was enhanced rate of dissipation. Out of the initial concentration of 10 ppm treatment, only about 3.46 ppm was available at the end of the first 2 hours, meaning that an amount of 6.53 ppm had been lost. The concentration of *p, p'*-DDE was minimal (0.5910 ppm) and that of *p, p'*-DDD was BDL (Table 10) as compared with the sharp decrease recorded. This unexpected decrease made another extraction to be done after the end of the experiment to determine the amount of pesticide residues, which could get adsorbed by the glass wall; for which a concentration of 0.01 ppm was realized. From this data it be can reported that concentration of 6.52 ppm is lost through evaporation to surrounding air, photodecomposition, volatilization (Wandiga *et.al,* 1996), and some is trapped within the framework of Faujasite Y cages (Yang *et. al*, 2006). After the 5th hour both *p, p'*-DDD and *p, p'*-DDE were detected with the concentration of *p, p'*-DDD increasing while that of *p, p'*-DDE reducing (Table 10). This is attributed to the degradation of *p, p'*-DDE to *p, p'*-DDD that could not be trapped by Faujasite Y because it had reached saturation as evidenced by constant concentration of *p, p'*-DDT from the 48th hour (Table 10) onwards. The concentration of *p, p'*-DDE increased at the end of the 22nd hour to the end of 120th hour and then dropped again, this is attributed to desorption and adsorption by the Faujasite Y. At the end of the experiment; 0.67 ppm of *p, p'*-DDT remained unchanged, 0.2654 ppm of *p, p'*-DDE and 0.3112 ppm of *p, p'*-DDD were formed therefore the major breakdown product is *p, p'*-DDD.

4.2.2.2 Fate of *p, p'*-DDT in Lake Victoria water treated with Faujasite X Zeolite

There was a decline in the concentration of *p, p'*-DDT upto 120th hour where BDL was recorded (Table 11). This loss is attributed to evaporation to the surrounding air, photodecomposition, volatilization as noted by Wandiga *et.al*, 1996, adsorption within the dimensionalities of Faujasite X cages (Yang *et. al*, 2006) and catalytic decomposition by the zeolite (Tanam *et. al,* 2006). The sharp increase was witnessed within the 2nd hour of the experiment. The concentration of *p, p'*-DDE increased at the end of the 2nd hour to the end of 5th hour and then dropped again, this is attributed to desorption and adsorption by the Faujasite X. At the 22nd hour the concentration of *p, p'*-DDE was BDL while that of *p, p'*-DDD was not detected throughout the experimental period. This could be attributed to catalytic decomposition by zeolite (Tanam et. al, 2006) and finally zeolite uptake (Yang et. al, 2006; Kanyi et.al, 2006). From the data, it can be reported that Faujasite X favors the formation of *p, p'*-DDE, which is again adsorbed within the zeolite matrix.

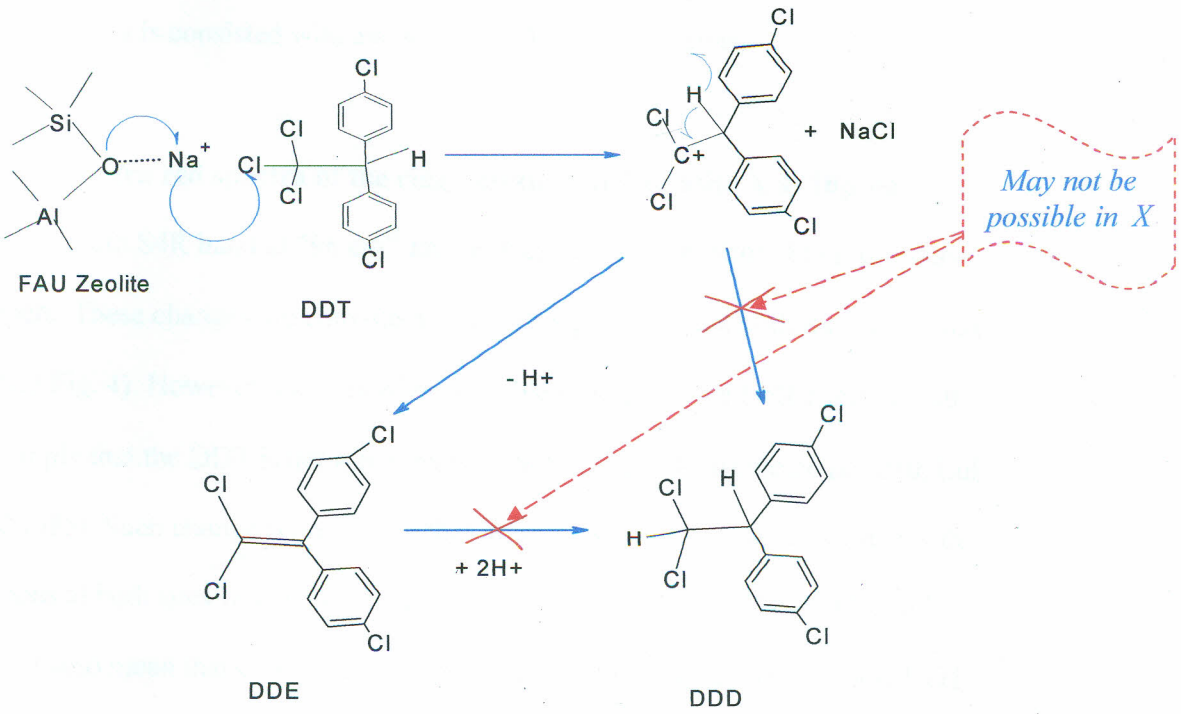
4.2.3 Chemo dynamics of *p, p'*-DDT degradation in Lake Victoria water under different treatments

The overall disappearance of *p, p'*-DDT residue has been found to be exponential. Partial log transformation of the data has aided in the calculation of the half-life value of the total residues in water. No linear relation can often be transformed to obtain linearity by log-log and semi log transformations. Using the product-moment correlation coefficient, r or the coefficient of determination R^2 checks linearity. The half-life value for dislodgeable residue of *p, p'*-DDT on the surface of treated water with Faujasite X zeolite is 6.1 hours while that of Faujasite Y zeolite is 9.6 hours. The low value of half-life for dislodgeable residues of *p, p'*-DDT on the water surface

shows that the *p, p'*-DDT disappears very fast from the surface water treated with Faujasite X zeolite than that of Faujasite Y zeolite. These are shorter than 145 days in field conditions in Nairobi (Lalah et, al. 1993), 56 days in fresh lake water (Wandiga, 1988) and 28 days in river water (USEPA, 1989). However no unambiguous comparison between the three studies can be made because the weather conditions under which the other study was carried out are not indicated. In any case the bound residues were not included in determining the half-life values obtained. The values compare well with the ones obtained in the present study.

4.2.4 Dehalogenation of organic halides using zeolite

Chlorinated compounds undergo dehydro halogenation and substitution dehalogenation. Most acidic protons associated with chlorine atoms cleave fastest (Kanyi et al. 2008). The super cage oxygen of NaX is considered weakly basic (Ortiz et al.1999) but Na^+ cations interact strongly with halogens.



Scheme 2: A possible breakdown mechanism for the DDT in presence of X and Y zeolites

The Y zeolite avails most of its H^+ for subsequent hydrogenation of the DDE to DDD. Such a reaction was restrained in the X due to the inherent paucity in the amount of H^+.

4.2.5. The infra red spectra of the ring vibration of Faujasite Y at 10ppm.

The shifting of S4R band at 796 cm^{-1} is consistent with a change in mass at the site III (See Fig. 4). In addition, the lack of changes for both the S6R and D6R bands at 750 cm^{-1} and 580 cm^{-1} respectively imply that the DDT is not affecting these sites directly. That is, neither the cations (Na+ ions) stationed at those sites nor the molecular DDT are interfered with in relation to the sites I and II (Kowenje *et, al.*2010). The above observed phenomenon demonstrate that when the NaY is exposed to the DDT, only some Na+ ions cited at site III are used up. It should be borne in mind that NaY is inherently bereft of Na+ ions at the site III. But more importantly the shift to lower wave numbers is consisted with anchoring of DDT at these sites.

4.2.6. The infra red spectra of the ring vibration of Faujasite X at 10ppm

For NaX, both S4R band at 796 cm^{-1} and S6R at 785 cm^{-1} are shifted to lower wave numbers. These changes are consistent with a change in mass at both the sites II and III (See Fig. 4). However, the lack of measurable change for the D6R bands at 580 cm^{-1} imply that the DDT is not affecting the site I directly (Kowenje *et, al.*2010; Lui *et, al.*1995). Such changes corroborate that in NaX, which is inherently awash with Na+ ions at both sites II and III; changes take place at these sites. These blue-shift changes also mean that more mass is added to these sites consisted with some DDT anchoring at the sites II and III.

4.2.7 The X ray diffraction (XRD) of Faujasite Y at 10 ppm DDT level

The reversal of the XRD relative intensities between the peaks at 10.12 and 11.90 2θ (Fig. 12), corroborates the redistribution of cations (Na+ ions) from one site (possibly in the sodalite) to another (possibly in the super cage) under the influence of DDT (Kowenje *et, al.*2010). Since no other strange additional peaks are observed in the XRD for Hyd NaY + DDT, it means that these Na+ ions are not relocating to any other sites but are being used up. This observation is consisted with the Ag-halogen confirmatory test which indicated that some reasonable amounts of Cl- ions are released in the process. These results are very consistent with the proposed mechanism in section 4.2.4

4.2.8 The X ray diffraction of Faujasite X at 10ppm DDT level

The reversal of the XRD relative intensities between the peaks at 10.12 and 11.90 2θ (Fig. 13), are more pronounced that those for NaY in Fig. 12. These changes are therefore consistent with the redistribution of cations (Na+ ions) from one site (possibly in the sodalite) to another (possibly in the super cage) under the influence of DDT (Kowenje *et, al.*2010; Salama *et, al.*2006). Again, since no other strange additional peaks are observed in the XRD for Hyd NaX + DDT, it means that these Na+ ions are not relocating to any other sites but are being used up. This observation is consisted with the Ag-halogen confirmatory test with indicated that some reasonable amounts of Cl- ions are released in the process. These results conform to the proposed mechanism in section 4.2.4. More importantly, here we observe that, more Na+ ions (45% changes) are used up in the reaction as compared to just 5% used up in the NaY.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the two types of zeolites used in this study i.e. zeolite X and zeolite Y, it was found that zeolite X was more effective in abstraction of p,p'-DDT pesticide residues. Considering the data presented in this report and those elsewhere in the literature, the conclusion drawn from this study can be summarized as below:

1. Zeolite do accumulate *p, p'*-DDT fairly well, therefore it can serve as a sizeable sink for pesticide residues

2. Zeolite X was found to be more effective than zeolite Y in removal of *p, p'*-DDT from water. Zeolite X treatment was found to have a half life of 6.1 hours while that of Y treatment was found to have a half life of 9.2 hours.

3. Degradation products in Zeolite X was only DDE while that of zeoliteY was DDE and DDD

4. The mechanistic pathway depends on the type of zeolite used.

5.2 Recommendations

1. Zeolites should be incorporated in water treatment to remove DDT and its metabolites

2. Comparison study should be done with other types of zeolite to establish which one is more effective than zeolite X

3. The same work should be tested with other persistent organochrorine or organophosphorus pesticides.

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