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Modelling the Photocatalytic Degradation Kinetics of Organochloride Chemicals in Aqueous Solutions

by

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ABSTRACT

Polychlorinated endocrine disrupting chemicals are environmental pollutants that are increasingly found in water sources. As a result of their hydrophobic properties, they generally accumulate in adipocytes of humans and wildlife when ingested. In this study, the feasibility of the advanced oxidation processes (AOPs) such as heterogeneous photocatalysis technology is investigated for the treatment of organochlorides in water systems. Titanium dioxide (TiO_2) is the semiconductor catalyst of interest. The literature suggests that the most prominent organochlorides in the region are organochloride pesticides (OCPs). A group of 5 compounds were identified for the investigation; DDT, DDE, heptachlor, chlordane, and a polychlorinated biphenyl compound named 2,3,4-trichlorobiphenyl.

Reverse phase solid phase extracted (RP-SPE) surface water organic analytes analysis was conducted using gas chromatography mass spectroscopy (GC-MS). Results from most sampling sites showed high concentration levels of the organochlorides in the environment. Heterogeneous photocatalysed mineralisation processes of organochlorides in aqueous systems were conducted in a batch reactor. Organochloride spiked solutions of differing catalyst concentrations are irradiated using a UV lamp for a period of 30 minutes. The reaction kinetics are determined and weighed against conventional photolysis. Results showed improved photo degradation of organochlorides under photocatalytic imposed conditions in comparison to photolysis. Results also suggest that photocatalytic degradation of organochlorides is less favoured with increased TiO_2 catalyst concentrations.

Enhanced catalyst performance studies through TiO_2 surface property modification were conducted using copper nitrate ($CuNO_3$) as a catalyst dopant. The doped catalyst showed slightly improved degradation of organochlorides at particular catalyst concentrations. Simulated photocatalytic rate of reaction kinetics results are in correlation with the modelled experimental results. They show variability of the degradation constant in the rate of reaction with varied catalyst concentrations. Catalyst concentration efficiency of each compound and the rate of the reactions were determined.

DECLARATION

I, **ZAKHELE KHUZWAYO,** hereby declare that all the work provided in this dissertation is to the best of my knowledge original (except where cited) and that neither the whole work nor any part of it has been, or is to be submitted for another degree at this or any other University or tertiary education institution or examining body.

SIGNATURE: …………………

DATE: …………………………

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LIST OF ABBREVIATIONS

ACTR	Activator of Thyroid and retinoid acid Receptor
AOP	Advanced Oxidation Processes
ASTDR	Agency for Toxic Substances and Disease Registry
CAR	Constitutive Androstane Receptor
$CaCl_2$	Calcium chloride
CBD	Central Business District
CdS	Cadmium sulphide
CO_2	Carbon dioxide
Conc	Concentration
CSIR	Council for Scientific and Industrial Research
$CuCl_2$	Copper chloride
$CuNO_3$	Copper nitrate
CuO	Copper oxide
DDT	Dichlorodiphenyltrichloroethane
DDE	Dichlorodiphenyldichloroethylene
DES	Diethylstilbestrol
DNA	Deoxyribonucleic acid
DWAF	Department of Water Affairs and Forestry
EDC	Endocrine Disruptive Chemical
EI	Electron Ioniser
EtoAc	Ethyl acetate
Fe_2O_3	Iron oxide/Ferric oxide
FID	Flame ionization detection
GaP	Gallium phosphide
GC-MS	Gas Chromatography/ Mass Spectrometry

GRIP1	Glucoccoticoid Receptor Interacting Protein 1
g/L	grams per Litre
He	Helium
HCl	Hydrochloric acid
HPLC	High Performance Liquid Chromatography
HS	Headspace
H_2O	Water molecule
IPCS	International Programme of Chemical Safety
IUPAC	International Union of Pure and Applied Chemistry
km	Kilometres
L	Litre
LC	Liquid Chromatography
LOD	Limit of Detection
MAA	MethoxyAcetic Acid
MeOH	Methanol
mg/L	milligrams per Liter
ML/d	Mega Litres per day
min	minute
mm	millimetres
$NaCl_2$	Sodium chloride
Na_2SO_4	Sodium sulphate
NR	Nuclear Receptor
OC	Organochloride
OCP	Organochloride Pesticides
O_2	Oxygen molecule
OH	Hydroxide

OPP	OrganoPhosphate Pesticides
PAH	Polynuclear/polycyclic Aromatic Hydrocarbons
PCB	Poly-Chlorinated Biphenyls
PCB 25	2.3.4-Trichlorobiphenyl
PXR	Pregnane Xenobiotic Receptor
rDNA	Ribosomal deoxyribonucleic acid
rRNA	Ribosomal Ribonucleic acid
rpm	Revolutions per minute
RP-SPE	Reverse Phase – Solid Phase Extraction
RT-PCR	Reverse transcriptase- Polymerase chain reaction
SPE	Solid Phase Extraction
SRC	Steroid Receptor Coactivator
SXR	Steroid Xenobiotic Receptor
TDS	Total Dissolved Solids
Ti	Titanium
TiO_2	Titanium dioxide
TIF2	Transcriptional Intermediary factor 2
TLC	Thin Layer Chromatography
TRAP	Thyroid hormones Receptor Activator Protein
UNEP	United Nations Environmental Programme
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
WWTP	Waste Water Treatment Plant
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide
ZnS	Zinc Sulphide

SYMBOL NOMENCLATURE

e^-	surface trapped valence band electron
h^+	conduction band hole
C	concentration of organic analyte (ngL^{-1})
C_i	initial concentration of organic analyte (ngL^{-1})
C_t	experimental concentration of analyte
C_c	catalyst concentration (mgL^{-1})
H^+	positive ion
K	Langmuir adsorption constant (ngL^{-1})
k_r	reaction rate constant (min^{-1})
k	rate constant (min^{-1})
t	time (min)

CHAPTER 1: INTRODUCTION

1.1 Background

Organochloride chemicals have been documented and demonstrated to be harmful to humans, wildlife and microorganisms due to their interference with the endocrine system. Organochloride compounds are a group of organic chemicals that are covalently bonded to numerous chlorine atoms. They are a subset of a wider class of compounds called Endocrine Disrupting Chemicals (EDCs). EDCs have various definitions including definitions that describe them as chemical compounds that interfere with the functionality of the endocrine systems of higher order organisms, especially animals. In the environment these chemicals generally originate from agrochemical products, designed primarily for pest control. These chemicals have been an inherent part of human livelihood for many years with documentation dating back several thousand years (Kaushik and Kaushik, 2007; WHO, 2002; Lunden and Noren, 1998; Cutkomp 1994). The most relevant and prominent class of endocrine disrupting compounds in the immediate environment of the Highveld region of South Africa are organochlorinated agriculturally applied compounds, the group of compounds intended for investigation in this study

Within the class of polychlorinated organic compounds are organochlorinated pesticides (OCPs) which are specifically produced to combat the attack of various pests on agricultural and horticultural crops, and polychlorinated biphenyls (PCBs) which are utilised as fire retardants. PCBs are produced as by-products of commercial processes and are present as complex mixtures containing multiple isomers at different degrees of chlorination. They are chemically inert and are used as chemical additives to oils for chemical stability (Ishikawa et al., 2007; ECDGE, 2004; WHO, 2000; UNEP, 1999).

Endocrine disruptive compounds commonly affect organisms in several ways, resulting in the inhibition of the targeted endocrine site (Bredveld et al., 2006; Tabb and Blumberg, 2006; Choi and Lee, 2004; Dawson, 2000). Some EDCs are natural occurring while the majority are introduced anthropogenically. The first known endocrine disrupting organochlorinated compound to be synthesised was dichlorodiphenyl trichloroethane (DDT) in 1874, even though it was only in 1939 when the insecticidal properties of DDT were discovered and later put to extensive use by military organisations against vector-borne diseases (WHO, 1979).

After DDT became commercially available, it was aggressively used in the agricultural sector. This led to a quick realisation of the potential harmful effects to wildlife and humans. Most countries imposed restrictions limiting production. Even though the restrictions have been in place for many decades, control beyond administered borders is still a universal challenge.

Due to the lack of control, organochloride chemicals application has propagated to levels difficult to quantify. This is evident from the broad nature of the environments these chemicals are found in; soils, sediment, atmosphere, and environmental waters. This study will attempt to investigate methods of environmental remediation.

1.2 Objectives

The objectives of the research were to: (i) determine the prominence of certain polychlorinated organic compounds in the aquatic environment of the Gauteng North region and promote a methodology to remediate areas with the highest sensitivity, such as drinking water sources; (ii) develop removal technologies for the organochlorides using reports in literature. Heterogeneous photocatalysis is the technique used, applying titanium dioxide (TiO_2) as a semiconductor metal oxide; (iii) investigate the efficiency of an oxidation enhancement method with the objective to achieve improved photocatalysis degradation of the organochloride compounds. This was attempted using copper oxide transitional metal ions to reduce the band gap energy of the catalyst through surface modification; and (iv) to determine the reaction kinetics involved in heterogeneous photocatalysis of the organochlorinated chemicals using different catalyst concentrations, and determine parameters that could be used in the scale up to pilot and prototype systems for degradation of different compounds.

1.3 Study significance

The study will quantify environmentally trapped organochloride chemicals and put into perspective the state of endocrine disruptive compounds in the immediate aquatic environment. The findings will divulge the significant health implications posed by organic chemicals dissociated in the aquatic environment. Provide an assessment of the viability of heterogeneous advanced oxidative processes using titanium dioxide as a metal oxide semiconductor. This study will also provide insight to the possibility of performance enhancement of the photocatalytic method through property modification. Copper oxide ion dopant will be used to surface modify the titania particle allowing for band gap reduction resulting in improved degradation efficiencies. Most importantly, this study will yield parameters which can be used for scale up and prototype systems for reactor design and optimisation for the remediation of water sites. Provide insight on the chemical behaviour of the compounds under study, and give fundamental background on the application of photocatalytic techniques in the mineralisation processes of many organic compounds found dissociated in aqueous systems.

CHAPTER 2: LITERATURE REVIEW

2.1 Organochlorinated compounds in the environment

Organochloride (OC) chemicals have been extensively used for pest control in agriculture, disease control in tropical areas and for chemical stabilisation in industries over the last century. The manufacturing of a class of these compounds called organochlorinated pesticides (OCPs) was extremely excessive upon the discovery of their insecticidal properties. Though hydrophobic, organochlorides are absorbed by soils and are partitioned into water. They enter the environment through rain water runoff and industry discharges. (Slabbert et al., 2008; Iwata et al., 2003; IPCS, 2002; Guruge and Tanabe, 2001). It has also been documented that significant organochloride contamination may result from atmospheric transportation, especially in industrialised areas with heavy air pollution. (Chevreuil et al., 1996; Iwata et al., 1995; Iwata et al., 1993).

Atmospheric pollution facilitates contamination of large areas in comparison to direct surface pollution. Studies by a number of researches including Concepcio´n and Lopez, 2003, Iwata et al., 1995, Iwata et al., 1993, Eisenreich et al., 1981, and others. As a direct result of recalcitrance to biodegradability and high dispersion coefficiency in water, OC compounds accumulate in sediment and soils (Awofolu and Fatoki, 2003; Brasher and Anthony, 1998; Iwata et al., 1995), Fig.2.1 elucidates the distribution of organic chemicals in the environment. The ocean acts as a terminal sink and accumulation has been elevated in recent years (Monirith et al., 2003; Guruge and Tanabe, 2001; Iwata et al., 1993).

2.2 Uptake of organochloride compounds from the environment

Organochlorinated compounds do not partition easily into aquatic phase due to their typically large molecular radii and low solubility's. OC compounds can be transferred through aqueous media through bioaccumulation as an alternative route (Concepcio´n and Lopez, 2003; Yamamoto et al., 2002; IPCS, 2002). Once they enter the biological food chains, they tend to bioconcentrate mainly because they are indestructible. In higher order organisms including humans, the main routes of entry are through ingestion and inhalation. Humans are continuously exposed to manufactured household products containing pollutants, with the aid of low quality building ventilation, indoors have become a significant source of these compounds (Weschler, 2009), and this is more prominent in households where building materials such as wood has been treated with chemical preservatives. Direct ingestion of OC from domestic and natural water accounts for another mode of uptake. Reclaimed water such as grey water may contain significant amounts of OCs mainly emanated from detergents and cosmetic products (Aneck-Hahn et al., 2009; Liu et al., 2009; Mahomed et al., 2008; Slabbert et al., 2008; Liu et al., 2004; Barcelo, 2003).

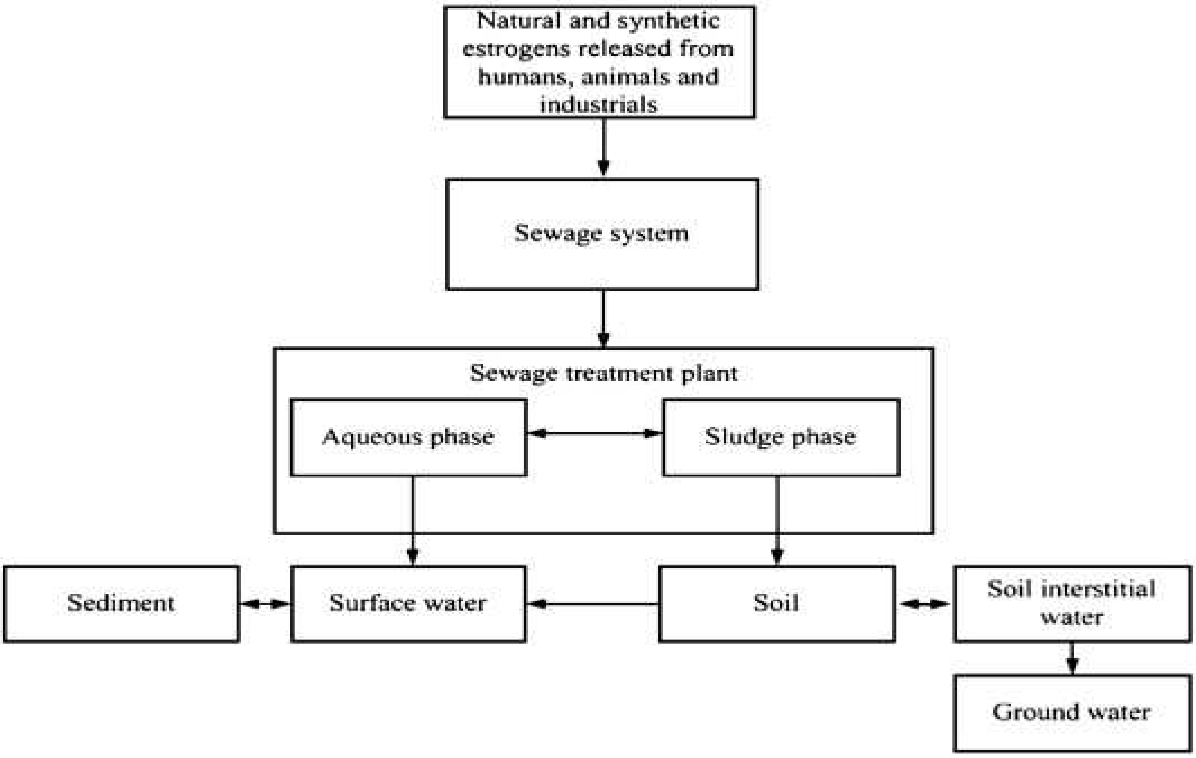


Figure 2.1: Endocrine disrupting chemicals distribution tree in the environment (Liu et al., 2009).

2.3 Structure and characteristics of organochloride compounds

Five organochlorinated compounds prominent in the environment have been identified for analysis in this study, namely: dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), chlordane, heptachlor, and trichlorobiphenyl (PCB 25). The structures of these compounds and characteristics are discussed briefly.

2.3.1 Dichlorodiphenyltrichloroethane (DDT)

DDT is by far the most popular and the OC that has been applied by humans in the past 50 years. It is a colourless and odourless solid crystal, hydrophobic and almost insoluble in any aqueous environment, completely soluble in lipids and organic solvents. DDT is conventionally used as an insecticide mainly against malaria, typhus, and certain other vectorborne diseases. It is stable under most environmental conditions, and is resistant to breakdown by enzymes present in most organisms (IPCS, 1979). The DDT structure in Fig.2.2 is formally known as 1,1-(2,2,2-trichloroethylidene)-bis(4-chlorobenzene) represented as (*p,p* - DDT). This structure has various isomers which make up what is accepted as DDT, consisting of 77 % (*p,p* – DDT), 15 % (*o,p* – DDT), the rest is made up of derivatives including DDE and DDD (IPCS, 1979).

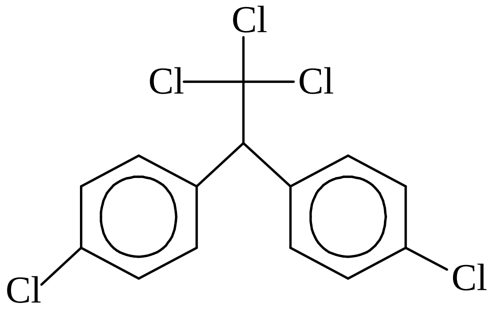


Figure 2.2: Chemical structure of dichlorodiphenyltrichloroethane

2.3.2 Dichlorodiphenyldichloroethylene (DDE)

The IUPAC name of DDE is 1,1-*bis*-(4-chlorophenyl)-2,2-dichloroethene. This compound is formed by dehydrohalogenation of DDT. DDE has similar properties and characteristics to DDT, it is also lipid soluble and concentrates in adipose cells (IPCS, 1979). Due to its stability in lipids, DDE is rarely excreted from the body, and body concentration levels tend to increase throughout life. The most significant mode of release of DDE from the body is through the excretion of breast milk, which delivers a substantial portion of the parents' DDE burden to the offspring (ASTDR, 2002). It is used as a pesticide in pest control, Fig.2.3 represents the DDE chemical structure.

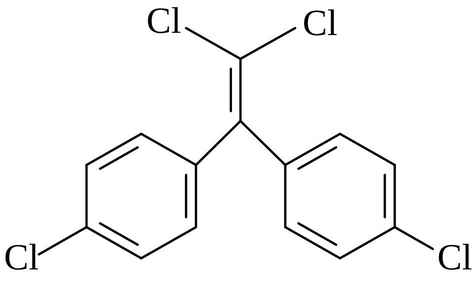


Figure 2.3: Chemical structure of dichlorodiphenyldichloroethylene

2.3.3 Chlordane

The IUPAC name of chlordane is 1, 2, 4, 5, 6, 7, 8, 8-octachloro-2, 3, 3a, 4, 7, 7ahexahydro-4,7-methano-1H-indene. It has several isomers, mainly contributed by cis and trans chlordane. Chlordane is almost completely insoluble in water, soluble in organic solvents and in lipid mediums. Chlordane is a yellow viscous liquid that is used as a versatile insecticide, mainly for non agricultural crops and animals. It has limited detectable odour and taste when dissolved in water, and resistant to chemical and biological degradation (IPCS, 1984a).

Chlordane originates from the United State of America, has been used for many decades as a broad-spectrum contact insecticide, mainly on non-agricultural crops and on animals. The main source of exposure of the general population is through residues in food. Chlordane is stable to light under normal conditions. In experimental animals, chlordane is readily absorbed via the skin and through oral ingestion (IPCS, 1984a).

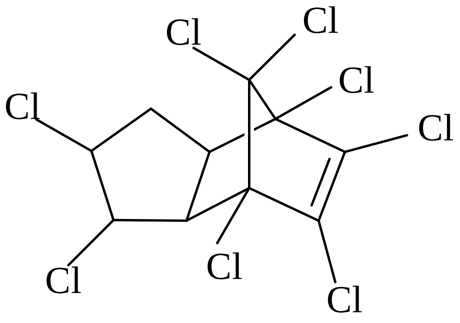


Figure 2.4: Chemical structure of chlordane

2.3.4 Heptachlor

The IUPAC name of heptachlor is 1, 4, 5, 6, 7, 8, 8-heptachloro-3a,4,7,7atetrahydro-1*H*-4, 7-methano-1H-indene. It is a white crystal with a camphor odour, completely insoluble in aqueous environments, and soluble in organic solvents. Heptachlor is oxidised biologically to heptachlor epoxide. It is mainly used as a pesticide agriculturally to terminate termites, ants and soil insects. A significant source of heptachlor is consumed through breast milk at infantile stages, it is also readily absorbed through skin contact, and following ingestion, heptachlor is transported throughout the body (IPCS, 1994; IPCS, 1984b).

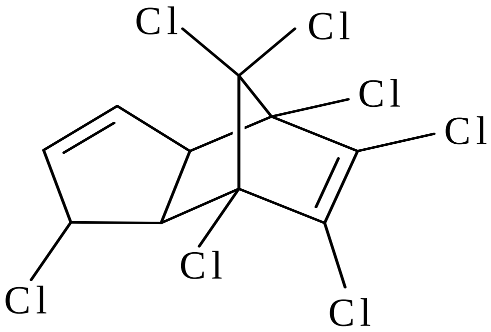


Figure 2.5: Chemical structure of heptachlor

2.3.5 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a very large and diverse group of compounds that form their own subclass of chlorinated hydrocarbons. They were discovered early in the 19th century and their usefulness was quickly recognised because of their unique physical properties. PCBs are manufactured commercially by progressive chlorination of biphenyl in the presence of suitable catalysts. The chlorination of biphenyl can lead to the replacement of 1-10 hydrogen atoms by chlorine, the conventional numbering of constituents positions is shown in Fig.2.6.

There are more than 200 theoretically possible chlorine conformations in this class of compounds. They have a wide range of uses, mainly concentrated in the area of dielectrics in transformers and capacitors, heat transfer and hydraulic systems, and are used in formulation of lubrication, cutting oils, in pesticides and in plasticisers. PCBs and their congeners have become widely distributed in the environment throughout the world, and are persistent and accumulate in food web. (IPCS, 1992; IPCS, 1976). The PCB of interest in this study is 2,3,4-trichlorobiphenyl (PCB 25).

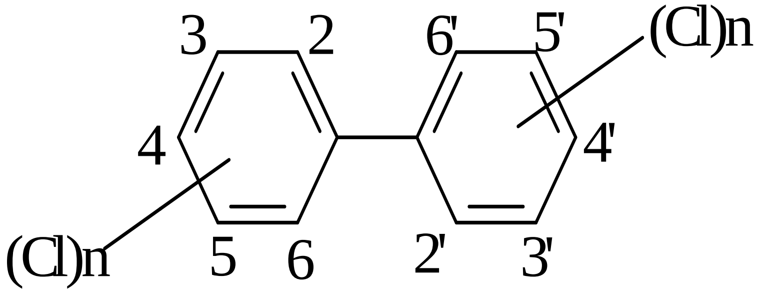


Figure 2.6: Chemical structure of PCBs. The possible positions of chlorine atoms on the benzene rings are denoted by numbers assigned to the carbon atoms.

2.4 Mechanisms of endocrine disruption by polyorganochloride compounds

Endocrine disrupting chemicals including OCPs and PCBs can act via multiple mechanisms and unpredictably so (Choi and Lee, 2004; Dawson, 2000). Even though these mechanisms are not understood thoroughly, they have been researched widely and new knowledge is still being discovered with more research. OCPs and PCBs generally interfere with receptor mediation of hormonal synthesis, transportation, and metabolism related mechanisms. These mechanisms are normally related to the perturbation of the endocrine function. Endocrine disruptors can generally be classified into: (i) chemicals that as a consequence of molecular structure bind to hormone receptors falsifying the action of natural compounds; (ii) chemicals that induce change in hormone concentrations through interference with synthesis and metabolic activities; and (iii) chemicals that interfere with signalling dynamics between different components of the hypothalamus pituitary endocrine gland axes (Bornman et al., 2007; Tabb and Blumberg, 2006; Choi and Lee, 2004; Dawson, 2000). Fig.2.7 illustrates the general actions of endocrine function inhibition, more specific modes of action will be discussed using Fig.2.8.

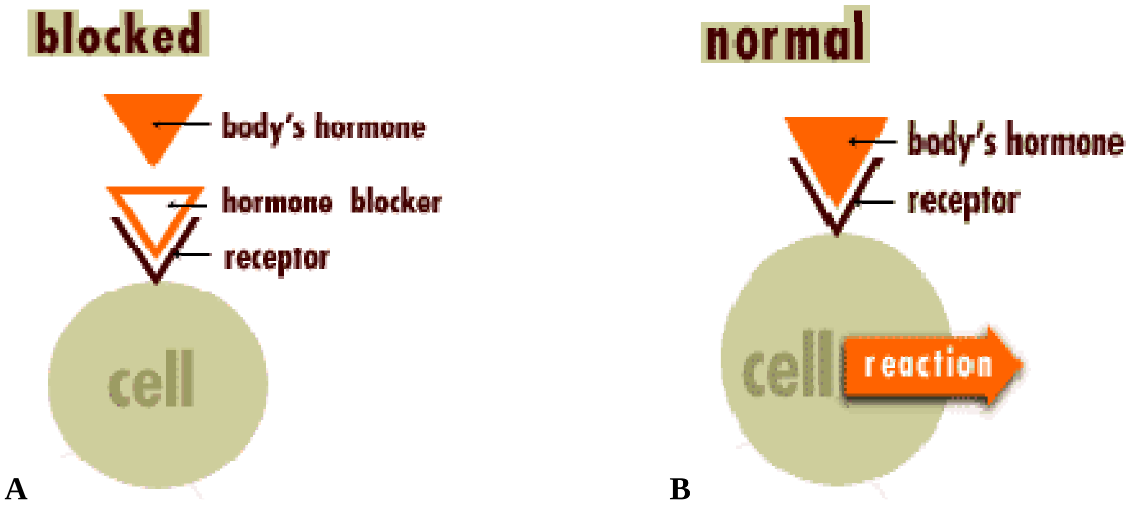


Figure 2.7: Illustration of the inhibition of normal (B) endocrine function by disruptive chemicals (A).

2.4.1 The alterations of endocrine disrupters at molecular level

Endocrine disrupters affect many hormonal pathways in organisms. Nuclear receptors are transcription factors which are found in most vital functions in mammalian organisms (Swedenborg et al., 2009). Endocrine disrupting compounds bind to these receptors via mechanisms evident in Fig.2.8 and induce various interferences deterring natural functions. The endocrine system includes a number of central nervous system pituitary target organs (Fig.2.9). There are potentially several target organ sites at which a given endocrine disrupting agent could disrupt endocrine function (Crisp et al., 1998). The altered functions include: (i) hormone synthesis (Swedenborg et al., 2009; Bretveld et al., 2006; Amaral Mendes, 2002; You et al., 2001; Crisp et al., 1998); (ii) hormone storage and release; (iii) hormone transport and clearance; (iv) hormone receptor recognition binding; and (v) hormone post-receptor activation (Bretveld et al., 2006; Amaral Mendes, 2002; Crisp et al., 1998). Endocrine modulation at target sites of the system will discussed briefly.

2.4.1.1 Endocrine disruption by modulation of steroid hormone metabolism

Steroids are a class of hormones that regulate many physiological functions of organisms such as sexual and reproductive development by acting on a variety of target sites (Tabb and Blumberg, 2006). Hormone availability is dependent on hormone biosynthesis, transport to the target tissue, levels of binding proteins, and hormone catabolism (Swedenborg et al., 2009). Undirected inhibition of synthesis of these hormones can result in detrimental effect to the organism. Specific receptors in organisms dedicated to regulation of different hormones can be altered, and many EDC compounds have been shown to increase the levels of endocrine disrupting metabolites while at the same time altering the local bioavailability of endogenous androgens and estrogens in humans (Xie et al., 2000). This provides a route through which EDC can alter steroid receptor activity without directly binding to steroid receptors (Tabb and Blumberg, 2006; Crisp et al., 1998). Fig.2.8 illustrates this modulation as it shows that alteration of steroid metabolism could contribute to the detrimental effects on the function of organisms. Two nuclear receptors, human steroid and xenobiotic receptor/rodent pregnane X receptor (SXR/PXR) and constitutive androstane receptor (CAR) are important regulators of xenobiotic and steroid hormone metabolism. SXR/PXR and CAR are highly expressed in the liver and intestine where they mediate the induction of cytochrome P450 enzymes (Tabb and Blumberg, 2006). Many known endocrine-disrupting organochloride compounds alter CAR activity and the expression of its target genes. As seen in Fig.2.8, the mediator complex function can be blocked by an EDC compound. Compounds such as DDT, DDE and PCBs have been documented to interfere with the mediator complex by blocking the nuclear receptors processes and increasing the transcriptional activity of both rat CAR and rat PXR (Wyde et al., 2003; Moore et al., 2002).

2.4.1.2 Endocrine disruption by modulation of nuclear receptors coactivators

Nuclear receptors are ligand regulated transcription factors that transduce steroid, retinoid and thyroid hormone signals into hormone regulated gene expressions (Han et al., 2009). EDCs can modulate target gene expressions by altering co-regulator and transcription factor levels. Nuclear receptors activate transcription by binding directly to hormone response elements in the regulatory region of target genes, recruiting a suite of coactivator proteins. Tissue specific differences in coactivator levels regulate nuclear receptor activation, as does general competition for coactivators among nuclear receptors and other transcription factors

(Swedenborg et al., 2009; Crisp et al., 1998). Chemical treatment has been shown to increase steady state nuclear receptor coactivator levels, thereby increasing transcriptional activation. Endocrine disruption results from competition between steroid receptors and xenobiotic receptors for transcriptional coactivators (Swedenborg et al., 2009; Tabb and Blumberg, 2006; Crisp et al., 1998). Fig.2.8 shows coactivators p160 (family that includes steroid receptor coactivator-1 (SRC-1), transcriptional intermediary factor 2 (TIF2)/glucoccorticoid receptor interacting protein 1(GRIP1), and activator of thyroid and retinoic acid receptor (ACTR)/amplified) and TRAP 220 (thyroid hormone receptor activator protein 220 (Tabb and Blumberg, 2006). Studies by Inoshita et al., 2003 and Min et al., 2002 demonstrated that many xenobiotic activators of CAR, and by implication SXR/PXR, may have endocrine disrupting effects on steroid hormone receptors by limiting coactivator availability.

2.4.1.3 Endocrine disrupters as hormone sensitisers

This particular endocrine disrupting mechanism does not mimic endogenous hormones, it instead increases the activity by altering cell signals that activate protein kinases or inhibit histone deacetylases (Tabb and Blumberg, 2006). Mechanistic studies by Jansen et al., (2004) show that xenobiotics chemicals function as both activators and inhibitors of histone deacetylases at doses that parallel known human exposure levels. These hormone sensitisers represent a new nuclear receptor interaction pathway relevant to endocrine disruption (Tabb and Blumberg, 2006; Crisp et al., 1998). Fig.2.8 shows that short chain fatty organic chemicals such as valproic acid and MAA (methoxyacetic acid) are responsible for endocrine disruption of this nature. Tabb and Blumberg, 2006 suggest that individuals who are exposed to these short-chain fatty acids are more likely to experience side effects from the administration of exogenous estrogens and progestins, including those given for oral contraception and postmenopausal hormone replacement therapy.

2.4.1.4 Binding of endocrine disrupters to nuclear receptors

Direct binding to hormone receptors is by far the most studied mechanism of endocrine disruption and is covered extensively in literature (Swedenborg et al., 2009; Crisp et al., 1998). Nuclear receptors are a large family of receptors that are involved in regulation of a wide range of physiological functions. Upon binding of a specific compound, their structural

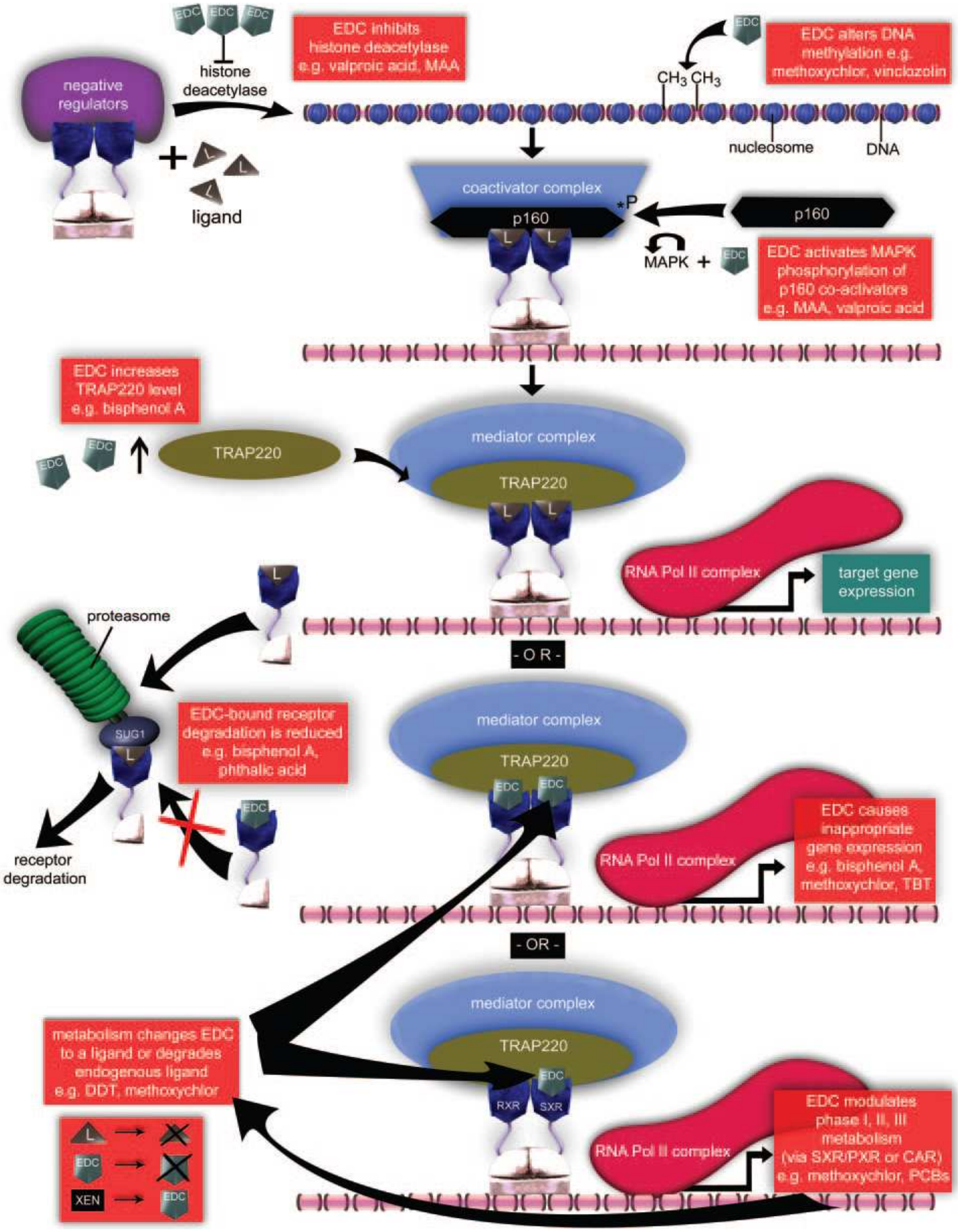


Figure 2.8: Representation of different modes of endocrine disruption, including: (i) modulation of steroid hormone metabolism; (ii) modulation of nuclear receptors coactivators; (iii) modulation of hormone sensitisers; and (iv) binding to nuclear receptors (Tabb and Blumberg, 2006).

conformations is changed and are transferred into the nucleus where they bind to corresponding responsive elements of DNA and trigger gene expression. Many nuclear receptors are physiologically activated by low molecular weight ligands (Janosek et al., 2006). A number of classes of receptors, namely, aryl hydrocarbon, estrogen, androgen, retinoid, and thyroid have been demonstrated in the above described manner. Each receptor has mechanisms by which it binds to ligands. The general principles of binding are briefly discussed:

1. Ligands binding to the aryl hydrocarbon receptor cause conformational changes resulting in its transportation into the nucleus. The aryl hydrocarbon dissociates from the complex and after dimerisation with aryl hydro-receptor the nuclear translocator binds to dioxin responsive elements regulating expression of specific genes (Janosek et al., 2006; Pollenz, 2002);
2. Estrogen receptors are a group of steroid hormones that play a key role in female hormone regulation and signalling, they are produced to a lesser extent in males. They are responsible for metabolic, behavioural and morphologic changes occurring during various stages of reproduction. Exceedingly high amounts of foreign compounds such as endocrine disrupting chemicals will result in negative effects. Estrogen levels are regulated by the hypothalamic-pituitary axis. The mechanism evident is similar to that of aryl hydrocarbons, only differing in the nature of the proteins present (Janosek et al., 2006; Crisp et al., 1998);
3. Androgen receptors are a group of compounds that play a similar role to that played by estrogen hormones in females, also produced by the hypothalamic-pituitary axis. They play a key role in the development of male primary and secondary sexual characteristics, act anabolically in stimulating protein synthesis, growth of bones and muscular mass amongst other functions. Several mechanisms of action are proposed for androgens, with the main being binding to androgen receptors and regulating it metabolism (Janosek et al., 2006; List et al., 2000);
4. Retinoid receptors are made up of vitamin A and its metabolites, they mediate important processes in organisms such as controlling growth, apoptosis and differentiation of embryonic cells, epithelial cells of gastrointestinal tract, skin and bones. Retinoid mechanisms of action act via basic nuclear receptors in three ways, using metabolisation of biotransformation enzymes that directly affect levels and function of retinoids, by disrupting binding of retinoids to retinoid binding proteins

using different metabolites, and by using xenobiotic chemicals to induced oxidative stress to disrupt levels oxidant agents of retinoids (Janosek et al., 2006); and

5. Thyroid receptors act as direct enhancers of metabolism via modulation of oxygen consumption and affect activities of other hormones like insulin, glucagon, somatotropin or adrenalin. They act through complex mechanisms involving several isoforms of thyroid receptors (Jugan et al., 2010; Janosek et al., 2006; Crisp et al., 1998).

2.5 The effects of endocrine disrupters to aquatic and wild life

There is significant documented evidence that a number of chemicals in the environment may disrupt the endocrine systems of aquatic and wild life. Through endocrine disruptive chemical properties of lipid solubility, these chemicals bioaccumulate and concentrate in aquatic animal tissue. This has been shown to have severe physiological effects to some organisms. These effects include: (i) abnormalities in thyroid function in fish, birds and mammal species (Mills and Chichester, 2005; Bosveld and van den Berg, 2002; Hutchinson and Pickford, 2002; Crisp et al., 1998); (ii) decreased fertility and reproductive abnormalities in fish, shellfish, mammals and related species (Barnhoorn et al., 2004; Guillette et al., 1994; Nolan et al., 2001; Crisp et al., 1998); (iii) decreased hatching success in fish, reptiles and birds species (Ankley et al., 2009; Crisp et al., 1998); (iv) demasculinisation and feminisation of fish, birds, reptiles, and mammals (Milnes et al., 2006; Kretschmer and Baldwin, 2005; Yokota et al., 2005; Bayley et al., 2002; Guillette et al., 1994; Crisp et al., 1998); (v) altered behaviour such as overt aggression and reduced predator avoidance in fish (McGee et al., 2009; Brian et al., 2005); and (vi) altered immune function in birds, mammals, and fish (Cai et al., 2009; Bolong et al., 2009; Hutchinson and Pickford, 2002; Crisp et al., 1998).

2.6 The effects of endocrine disrupters to human health

The most elucidated evidence of estrogenic effect to human health is in female reproductive and developmental systems, although substantial research has been conducted to associate occupational exposure to pesticides with fertility problems in men (Bredveld et al., 2006; Amaral-Mendes, 2002). Though not much direct determination research has been conducted on human subjects, there is enough knowledge subsidised by animal studies to validate potential harmful effects on humans by endocrine disrupting chemical compounds. Fig.2.9 represents the human endocrine system, which is essentially a controlled network of hormone releasing glands to regulate bodily functions. Epidemiologic studies have found associations between exposure to specific endocrine disrupters and paralleled effects on humans (Filby et al., 2007; Amaral Mendes, 2002; Solomon and Schetter, 2000). Different subdisciplines of research have dedicated efforts to the understanding of chemical toxicology to humans and wildlife at molecular levels, these disciplines function at different scopes within the arena of toxicology. According to Phillip and Foster (2008) and Patisaul and Adewale (2009) they include: (i) genomics, the structure and function of genomes, it generally involves analysis of DNA sequences; (ii) proteomics, the technologies that quantifies changes in the levels and status of individual proteins under different conditions; (iii) metabolomics, quantification of changes in cell metabolism by measuring primary and secondary metabolites using various methods; (iv) neurotoxicology and neuroinformatics, fields that parallel neurobehavioral toxicity and human responses (Phillip and Foster, 2008).

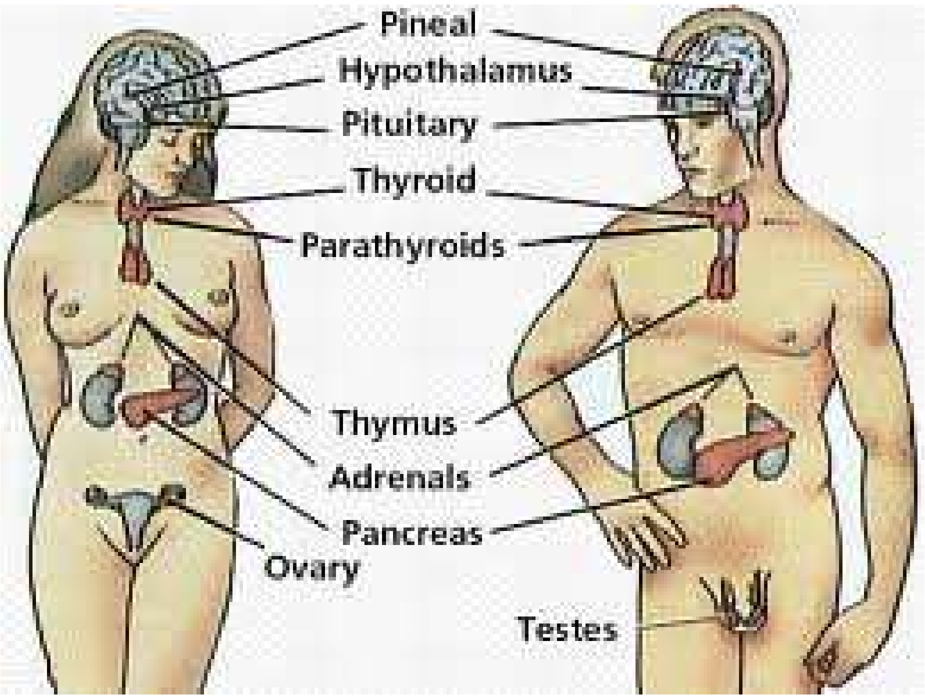


Figure 2.9: Human endocrine system, the network of hormone releasing glands.

Known effects of endocrine disrupters on human reproductive systems predominantly involve abnormalities in fertility of females and to a lesser extent infertility of males. Subfertility is the more accepted classification amongst human subjects for the inability to conceive within a specified period, generally 12 moths. There are four understood subfertility disorders, given by Bredveld et al., (2006) as: (i) male subfertility, the reduced ability of the female partner to become pregnant. This may be due to low sperm concentration, reduced motility and or abnormal morphology of sperm; (ii) ovulation disturbances, these are problems that present themselves as irregular or absent menstrual periods and can be substantiated through measurement of reproductive hormones; (iii) defects in spermatozoa-cervical mucus interaction, preventing sperm from reaching the oocyte; and (iv) tuboperitoneal disorders, damage or obstruction, hydrosalpinx, pelvic adhesions, and endometriosis.

Knowledge of endocrine disrupting effects on human health beyond postnatal stage is not abundantly documented. A few studies have been conducted related to this subject, documented health effects associated with endocrine disrupters include cryptorchidism and hypospadia, which is the developmental defect marked by the failure of the testes to descend into the scrotum. The common cancers such as testicular, prostate, and breast, and endometriosis, which is characterised by aberrant growth of endometrial cells outside the uterus and ensuing dysmenorrhea, can also be attributed to EDCs (Bredveld et al., (2006); Aramel-Mendes, 2002; Juberg, 2000). According to ISEA (2002, pp S198), menstrual cycle disturbances in females can also be subsequent results of endocrine disrupter exposure. Teilmann et al., (2002) documented the effects of endocrine disrupters on pubertal development in children.

2.7 Water bodies as a source of organochloride pollutants

Irrigation, rain water runoff, landfill sites and unmonitored industrial discharges make up the main sources of organochloride pollutants that find refuge in water bodies. Pollutants may undergo long range transport to reach designated water bodies such as dams, rivers and lakes. Surface water in the Gauteng North has been documented containing various estrogenic substances present, including organochloride substances (Aneck- Hahn et al., 2009; Zhang et al., 2009; Slabbert et al., 2008; Bornman et al., 2007). Organochloride pollutants detected in a number of water bodies around the Pretoria area, were speculated to be sourced from the nearby wastewater treatment plants (WWTP) (Mahomed et al., 2008). Another study conducted by Aneck-Hahn et al., (2009) in Limpopo suggested that estrogenic activity in surface water related to industrial discharge is common, platinum mines are prominent in the area studied. Many studies have and are being conducted with the concern of water bodies being the site that harbour endocrine disrupting compounds (Bolong et al., 2009; ISEA, 2002; Hutchinson and Pickford, 2002; Guruge and Tanabe, 2001; Brasher and Anthony, 1998).

2.8 Organochloride pollutants in wastewater-local relevance

EDCs in drinking water are an issue of great concern. Existing water treatment facilities are not equipped to deal with unidentified contaminants (Bolong et al., 2009). Their recent emergence challenges the conventional water treatment technologies in dealing with undesired compounds. Due to the diversity and complexity of EDCs, numerous processes and techniques may be required just to achieve removal of a single class of compounds. Table 2.1 list types of endocrine disrupting pollutants typically found in environmental waters. There are over 80 000 chemicals registered for chemical use, and it is still unclear how many are of potential harm to the endocrine system (WHO, 2002).

Wastewater treatment is more complex than conventional water treatment, as it contains a much great range of pollutants. This point source generally provides indication of the state of environmental with regards to organic pollution. Slabbert et al., (2008) conducted a study investigating the estrogenic activity in three treatment plants in the Gauteng region. Results showed estrogenic activity in treated and untreated water. Another study by Bornman et al., (2007) in the same region revealed that endocrine disrupting chemical such as PCBs were prominent in the surface waters. Evidence has been documented of the ineffectiveness of wastewater treatment physicochemical processes in removing EDCs (Westerhoff et al., 2009; Bolong et al., 2009; Adams et al., 2002).

2.9 Treatment and removal of OC compounds

Since the establishment of water and wastewater treatment as a discipline, various techniques have been attempted and applied with the objective of providing safe and clean usable water.

The emergence of organic micropollutants in the aquatic environment has introduced different challenges to known and applied methods of water cleansing.

Table 2.1: Types of endocrine disruptive chemicals

Endocrine disruptors	Descriptions of compounds
OCPs	Organochloride Pesticides are still widely used in SA, especially in areas where malaria prevails.
Phthalates	Add flexibility to a large range of plastic goods. Also found in some paints, inks, adhesives and cosmetic products.
Bisphenol A	Used extensively in the production of polycarbonate and epoxy resins. It can also be found in adhesives, reinforced pipes, interior coatings of tins and drums, flooring, electronic goods, powder paints, lenses, crash helmets, thermal fax paper and some resistant plastic foods and drinks containers. P-nonylphenol: Found in industrial and household detergents.
DES	Diethylstilbestrol was the first synthetic oestrogen to be developed. It has traditionally been used by pregnant women to prevent miscarriages.
PCBs	Polychlorinated Biphenyls have historically been used as coolants and lubricants in transformers, capacitors, and other electrical equipment.
Atrazine	Is still widely used in South Africa as a herbicide, especially in the maize producing areas.
Dioxin	By-product of industrial processes, including waste incineration, food containment.
Estradiol	Form of oestrogen used to treat, for example, symptoms of menopause.
OPP	Organophosphate Pesticides includes chlorpirifos, Azinfos-methyl and Parathion.

One of the major challenges being that each compound or certain classes of compounds may require specific technologies for treatment when dissolved in water. This concern is further exacerbated by the fact that treatment using convectional technologies yields recalcitrant chemical derivatives with properties of possible harm to organisms. Recent research in the scientific community has deemed technologies that completely mineralise pollutants more viable. These techniques utilise chemical oxidation processes resulting in noble constituents. They are generally classified as advanced oxidation processes (AOPs).

There are a range of AOPs reported in the literature dealing with treatment of water pollutants. They include catalysis, electrochemical, Fenton's reagent, ferrate ionising radiation, microwave, photo Fenton's reagent, and photocatalysis. Some of the processes are commercially applied to full scale while others are being tested at pilot scale and at laboratory bench levels (Parsons, 2004; Andreozzi et al., 1999; Akmehmet-Balciouglu and Arslan, 1998; Hoffmann et al., 1995). Among the AOPs mentioned, heterogeneous photocatalysis utilising a semiconductor catalyst (TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS) has yielded the most promising efficiencies in degrading a wide range of organic pollutants in the environment. Photocatalysis is so far the only chemical method that has been demonstrated to completely mineralise organic compounds to water and carbon dioxide under ambient operational conditions. In this process, a chemically inert semiconductor metal oxide is used as catalyst to generate oxidative oxygen species such as OH° and O° radicals. Heterogeneous photocatalysis has been uniquely useful in wastewater and water application as a result of some important features, such as: (1) low operational cost and ease of operation of the method; (2) standard operating temperatures and pressure; and (3) complete mineralisation achieved without by-products formed. The major practical drawback of the application of semiconductor photocatalysis is the difficulty in recovery or separation of the catalysis from the treated solution. This has hindered practical industrial applications. Another factor posing a challenge is the limited theoretical understanding of the common reactor operational parameters, and the system interactions, which are causing difficulty in process optimisation. There are various commercially available semiconductors, some of which were mentioned earlier in this report. Titanium dioxide (TiO_2) is the most commercially used, as it offers unique principles, including: (i) high activity; (ii) significant stability to light illumination; (iii) low cost; and (iv) non-toxic and remains stable after repeated catalytic cycles (Parsons, 2004). Titanium dioxide absorbs light in the visible or low-energy range (300-370 nm) of the ultraviolet regions of the spectrum. The mechanism of photocatalysis and the band gap produced is well documented by Vinod and Anirudhan, 2002; Peral et al., 1997; Hoffmann et al., 1995; Linsebigler et al., 1995; Fox and Dulay, 1993. A diagrammatic illustration of the band gap production mechanism is represented in Fig.2.10. This figure essentially depicts the mechanism of the electron-hole pair formation with illumination of the titania particle surface, the complete mechanism will be better elaborated in chapters to come.

Illumination of TiO_2 by irradiation with energy equal to the band-gap energy or larger elevates electrons in the valence band to the conduction band is represented in Eq.2.1;

$$TiO_2 \rightarrow e^- + h^+ \qquad (2.1)$$

where e^- and h^+ represent the surface trapped valence band electron and the conduction band hole respectively. Naturally the produced electron and the resultant positive hole can recombine immediately after photo-induction. This is a very quick reaction which prevents the reduction oxidation reactions. To get around this challenge, an electron scavenging species is used to interfere with the recombination process. Eq.2.2 represents the scavenging process conducted by oxygen while allowing for oxide radicals formation.

$$e^- + O_2 \rightarrow O_2^- \qquad (2.2)$$

It should be noted that all the chemical interactions that take place in photocatalysis are not possible without the presence of water molecules in addition to the dissolved oxygen. Water is responsible for the formation of the highly reactive hydroxyl radicals, that are essential in the degradation and mineralisation process, this reaction is presented in Eq.2.3.

$$h^+ + H_2O \rightarrow OH^\circ + H^+ \qquad (2.3)$$

The OH° radical produced facilitates the mineralisation of the compounds into noble constituents represented as CO_2 and H_2O in Eq.2.4, where OC depicts an organochloride compound.

$$OH^\circ + [OC] \rightarrow CO_2 + H_2O + [Cl^- \text{ constituent}] \qquad (2.4)$$

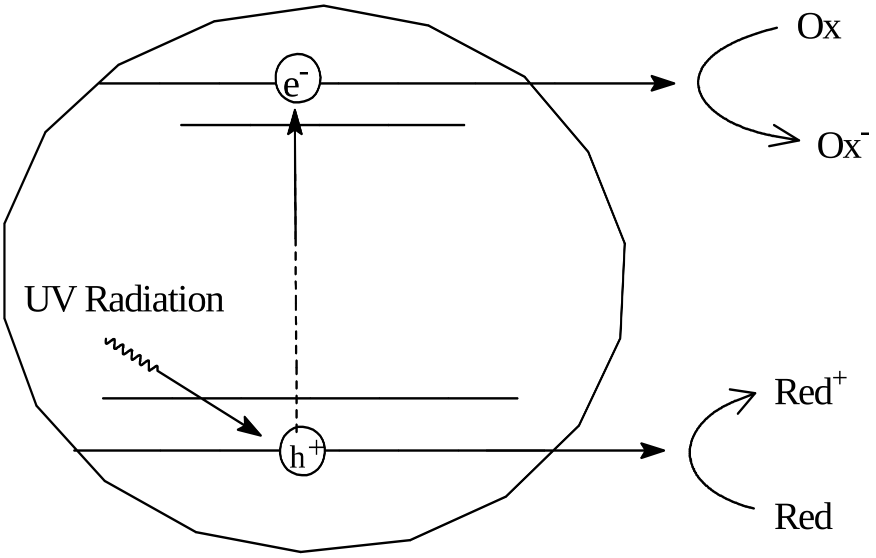


Figure 2.10: Schematic diagram of band gap produced during semiconductor illumination.

Complete mineralisation is not necessarily a direct process. Corresponding organic intermediates are produced in photocatalysis. Given enough time of the irradiation process it can be expected that complete mineralisation can always be achieved. Eq.2.4 can be slightly modified to yield Eq.2.5,

$$OH^{\circ} + [OC] \rightarrow Intermediates \rightarrow CO_2 + H_2O + [Cl^- \, constituent] \qquad (2.5)$$

where the intermediates can also exist in solid form.

The common technologies for the implementation of heterogonous photocatalysis include: (i) suspended systems, where the catalyst is in a form of suspended powdered slurry in water; (ii) fixed support systems, where the catalyst is embedded on a support surface material such as pyrex; and (iii) surface modified catalyst, to improve the performance of the catalyst by increasing its surface area to volume ratio and reduction in band gap energy. Numerous technological advances have been attempted, these include, surface modification using transitional metal oxides, nano particle size catalysts processing, and advancement in immobilisation and supports such as synthetic clays (Chong et al., 2010). Heterogeneous photocatalysis in this study will be attempted using TiO_2 semiconductor suspended in a chemically spiked aqueous slurry manor.

2.10 Chapter Summary

This chapter aimed at elucidating the dangers poised by endocrine disrupting chemicals to organisms. It identified organochlorides as one of the classes responsible for endocrine disruption. Water was shown to be the medium that transport the majority of pollutants in the environment. In the environments OCs are leached from soil and sediment, sourced from agricultural chemical application. The properties of the OCs of interest were presented to justify the need to deal with these recalcitrant chemicals.

The different facets of the endocrine system and how it is affected by OCs at molecular levels was reviewed using available literature. Probable mechanisms of disruption at nuclear functional levels were identified to elucidate the direct relation of the dangers to humans and wildlife. The study primary objective is to identify technological applications of OCs treatment and removal in water. One method that boasted principles of efficiency and applicability was found to be heterogeneous photocatalysis. The literature demonstrated the titanium dioxide catalyst to be the most chemically viable semiconductor. It can achieve complete mineralisation of OCs under mild conditions.

CHAPTER 3: MATERIALS AND METHODS

3.1 Environmental water sampling

Water samples from three wastewater treatment plants and three dams in the Gauteng North region were collected in the summer period. The samples were intended for collection proceeding heavy Highveld summer rainfalls. The hypothesis made was that applied agrochemicals percolate into lower soil and sediment depths upon irrigation. They sit in this intermediate region undisturbed and accumulate over time. Their dissolution is only likely to be achieved through aggressive penetration. Highveld early summer rainfalls generally result in flood type conditions, it was hypothesised that embedded chemicals at shallow depths would be accessed and carried in the leachate allowed by the excess water. The water samples were expected to be the sum of short and long term contamination in soils and fresh entry pollutants.

3.1.1 Sample collection source information

Wastewater Treatment Plant A

It is located on the southern banks of the Apies River on the north-western edge of the Pretoria Central Business District (CBD). Collects waste from central Pretoria using mainly the outfall sewer. Treats approximately 60 ML/d of wastewater

Wastewater Treatment Plant B

Treatment plant B is situated on the eastern bank of Pienaars River about 40 km from eastern Pretoria. It is located north of Mamelodi Township and south of Roodeplaat Dam. Influent is mainly sourced from varying surrounding projects including agriculture and correctional services facilities. It has hydraulic design capacity of 62 ML/d but receives about 45 ML/d.

Wastewater Treatment Plant C

Treatment plant C is also located approximately 40 km east of Pretoria. It is situated immediately to the west of the Roodeplaat Dam and discharges effluent into the dam. The surrounding area comprises of mainly agricultural farmlands. This plant has a design capacity of 35 ML/d.

Dam 1

This dam is in the Bojanala Region of the North West Province, about 100 km from Central Pretoria. It is surrounded by the Magaliesberg mountain range. The current dam's capacity is 205 million cubic metres and its shoreline, when full, is about 56 km. It is recreationally used for para-sailing, windsurfing, water and jet skiing. The dam has been renowned for poor water quality, has high concentrations of phosphates and nitrates sourced from the Crocodile River, the major inflow, resulting in significant eutrophication. The primary pollution sources are industrial and domestic effluent from Gauteng.

Dam 2

It is a concrete arch dam situated on the Pienaars River about 40 km from eastern Pretoria. The dam was originally intended as an irrigation dam, but later became a popular recreational spot. WWTP B and C both feed into this dam, resulting in highly eutrophic conditions. The current capacity of this dam is 40 million cubic metres.

Dam 3

This dam is located in the Rietvlei nature reserve, which is in the city limits of Pretoria. Supplies 10 million Litres of drinking to Pretoria, and has a capacity of 12 thousand Litres. The surrounding environment is generally reserve property harbouring wildlife. Reserve activities include horse rides, hiking trails, angling and camping.

Sampling from all sites was conducted late November 2010, a week proceeding relatively heavy rain falls in the region. Wastewater sampling was conducted at three points of the treatment processes; post screening and grit removal, post secondary clarification, and after disinfection and chlorination. Dam sampling was done at random accessible shoreline points. Samples were directly collected into 5 Litre transparent glass containers and stored in a refrigerator at 4 ˚C until analysis. Table 3.1 has the summary of the sampling points and the designated sample identities.

3.1.2 Water and wastewater sampling information

Table 3.1: Water and wastewater sampling information

Sample Collection	Sample Source	Sampling Point	Sample Identity
1	WWTP A	Influent	A1
2		Post Clarification	A2
3		Effluent	A3
4	WWTP B	Influent	B1
5		Post Clarification	B2
6		Effluent	B3
7	WWTP C	Influent	C1
8		Post Clarification	C2
9		Effluent	C3
10	Dam 1	Shoreline	DAM 1
11	Dam 2	Shoreline	DAM 2
12	Dam 3	Shoreline	DAM 3

3.2 Chemicals and reagents

Organochloride pesticides (OCP) and polychlorinated biphenyl (PCB) were purchased from Sigma-Aldrich Logistik GmbH (Schnelldorf, Germany). Analytical solvents, ethyl acetate (EtOAc), methanol (MeOH), and hydrochloric acid (HCl) as well as sodium chloride (NaCl) and copper nitrate ($Cu(NO_3)_2.3H_2O$) salts were purchased from Merk (South Africa). Aeroxide P25 anatase Titanium Dioxide was purchased from Evonik Degussa GmbH (Japan). Solid phase extraction (SPE) Strata C18 E (55 µm, 70A) 500 mg/6mL were obtained from Phenomenex (Separations, South Africa). Ultra pure (UP) water was dispensed by the Millipore Direct Q3 with pump instrument. Whatman no1 filter paper (110 mm) purchased from Merk (South Africa)

3.3 Conductivity, salinity, Total Dissolved Solids (TDS), and pH analysis

Conductivity, salinity, and TDS were measured at ambient temperatures using a Thermo Orion 125+ metre. The pH was measured using a Hach HQ11d metre, the instrument was calibrated using pH 4 and 7 buffer solutions. Samples were filtered using Whatman no1 filter paper (110 mm) in a buchner funnel using a Beoco R300 (Germany) pump.

3.4 Extraction of environmental water

Water samples were processed according to the following procedure: 100 mL samples filtered using a pump to accelerate separation. The pH of each sample was adjusted to 3 units using concentrated HCl, and conductivity adjusted to approximately 50 mS by adding NaCl. SPE cartridges were conditioned with 3 mL EtOAc followed by the application of 3 mL MeOH, and washed with 5 mL of UP water. Without drying, water samples were passed through the cartridges under vacuum. The cartridges were then dried for 2 hours in a 50˚C incubating oven, analyte compounds were then eluted using 3 mL of MeOH.

3.5 Photocatalysis SPE extraction method

SPE cartridges were conditioned with 3 mL of MeOH, followed by 5% (v/v) MeOH-Water organic modifier, and washed with 5 mL of UP water. Without drying, 1 mL aliquots experimental sample was passed through the cartridges. The cartridges were then dried for 2 hours in a 50˚C incubating oven, analyte compounds were then eluted using 3 mL of MeOH.

3.6 Preparation of stock and calibration curve working standard solutions

Stock solution of analyte compounds at concentrations of 1 and 0.5 µg/L were prepared by weighing appropriate amounts of each into 100 mL glass volumetric flask, dissolved with GC grade MeOH, sealed and stored in the refrigerator at 4˚C. Five-point calibration concentration plot for each compound ranging from 10 to 250 ng/L were prepared by adding the appropriate volume of stock solution, made up with MeOH.

3.7 Preparation of photocatalysis experimental working solutions

Experimental working solutions were prepared by adding 10 mL analyte compounds stock solution to a 100 mL volumetric flask, and making up the volume using UP water. Appropriate masses of anatase-titanium dioxide particles were added to the solutions to achieve concentrations of 0, 5, 10, 30, 50, and 200 mg/L TiO_2, and stirred for 10 minutes.

3.8 Preparation of copper oxide doped catalyst solution

Titanium dioxide (TiO_2) surface was modified by loading copper onto the surface. The copper ions (Cu^{2+}) were reduced photocatalytically using copper nitrate attached to three waters of crystallisation ($Cu(NO_3)_2.3H_2O$). The procedure was as follows: 1 g of TiO_2 was added to 50 mL of copper solution with a concentration of 30 g/L in ultra pure water. The mixture was sonicated for 30 minutes to disaggregate the particles, and magnetic stirred for twenty hours at room temperatures (below 25 ˚C). Centrifuged at 6000 rpm for 30 minutes, repeated rinsed with UP water until blue colour disappeared. Dried in oven at 110 ˚C for 20 hours, and the resulted solid was grinded to achieve smaller radii particles.

A copper doped powdered TiO_2 catalyst equivalent to concentrations of 10 and 30 mg/L was dispensed into the experimental solutions, and magnetically stirred for a period of 10 minutes before illumination. It was noticed that the grinded titanium oxide particles sizes were not replicable to the original sizes of raw anatase titanium dioxide, and it was also observed that the doped particles submerged to the bottom of the solution and did not distribute equally in solution. A hypothesis was formulated that the larger size particles would not be as effective in the photocatalytic oxidation of the chemicals. A paired experiment was conducted, where in one experiment the resulting copper dopant experiments solution were sonicated to finer sized particles for 5 minutes before photocatalysis, and in the other experiments raw grinded copper dopant was used directly.

3.9 Instrumentation

Water samples were analysed using a PerkinElmer Gas Chromatography (GC) system comprising of a Clarus 600 GC, and a Clarus 600 T Mass Spectrometer (MS) (PerkinElmer, South Africa division). The GC system injector consists of a split/splitless injector (CHP), a temperature programmed split/splitless injector (PSI), and a temperature programmed on column injector (POC). Sample injection achieved by a multi-mode autosampler comprising of 82 vial multi injection automated rack, uses 50 µL syringe. Chemical separation component was the Elite 5MS GC system capillary column (30 m, 250 µm) from PerkinElmer. Carrier gas was Helium (He) of 99.999% purity and applied at a flow rate of 1 mL/min. MS interface has an Electron Ioniser (EI), a high performance mass analyser, and a detector consisting of a dynode, phosphor plate and photomultiplier tube. Instrument is ultra tuned weekly to optimise parameters, and mass calibrated quarterly.

3.10 GCMS analysis

Sample volumes of 0.5 µL were injected into the GC system operating at a fast injection speed, injection port temperature was set at 250˚C. The column oven program was: initiated at 100˚C (not held) → ramped at 15˚C per minute until 280˚C. Carrier gas split flow of 3 mL/min and a flow rate of 1 mL/min. The MS method was operated using Electron Ionisation (EI^+) mode, centroid data setting. Scan duration set at 0.3 seconds and inter scan delay at 0.2 seconds.

3.11 Kinetic simulation and statistics

Aquasim 2.0, a computer program was used for the identification and simulation of aquatic systems. Sigmaplot 11 technical graphing and statistical programs was used to perform graphical calculation and statistical calculations.

3.12 Reactor design and procedure

The reactor as shown in Fig.3.1 is composed of a jacketed glass beaker containing a continuously stirred aqueous experimental analyte solution, and submerged into the solution are compressed air bubbling tube and sampling tube. The glass beaker was rested on a magnetic stirrer instrument from Labex FMX electronics (STR-mH). The glass beaker water cooling jacket was linked to a MasterFlex console drive pump from Cole-Parmer instruments (Easy Load II) driving cooled water into the beaker from an ice bucket.

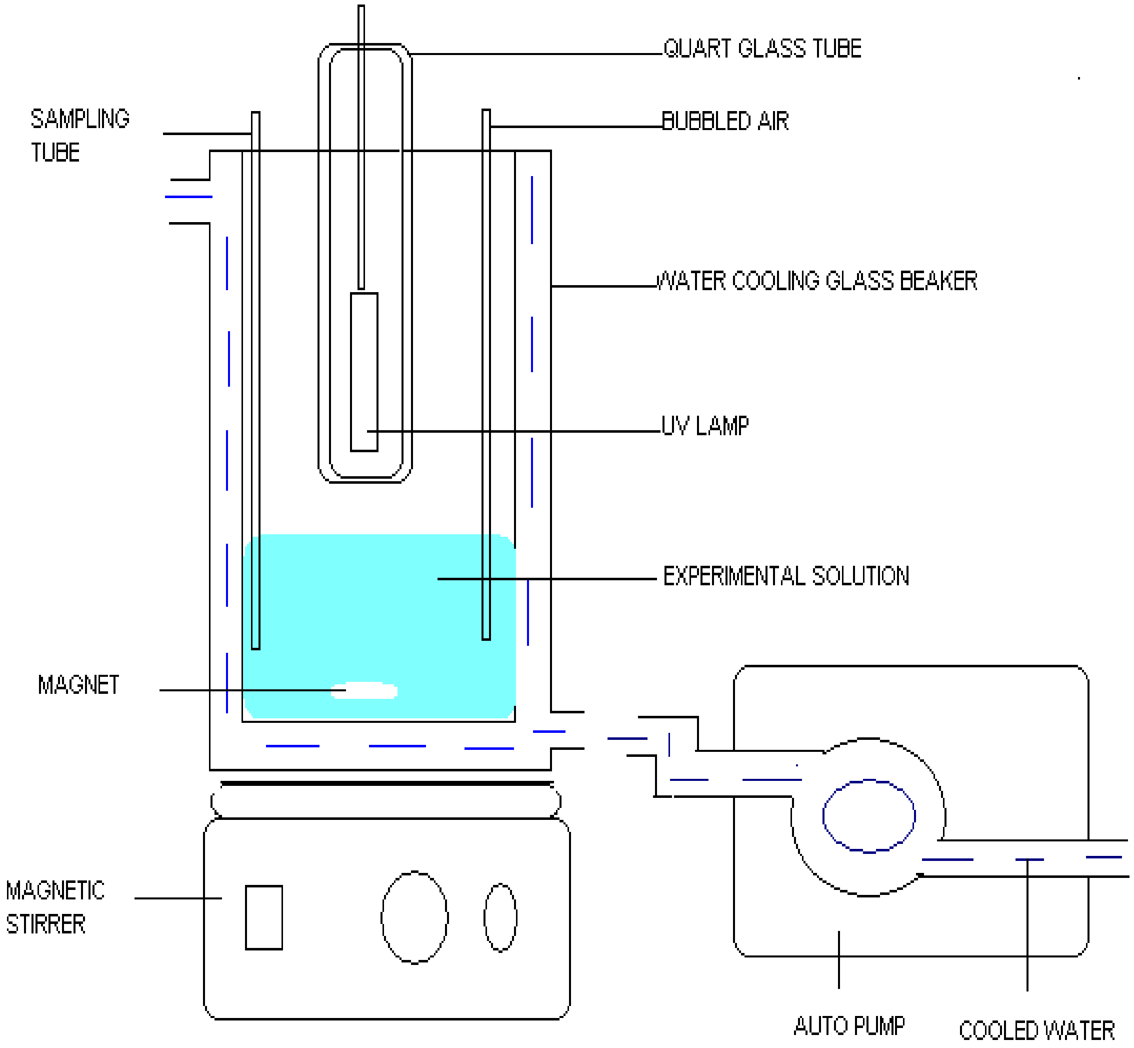


Figure 3.1: Schematic diagram of the photocatalytic reactor

Suspended in the glass beaker space above the water surface was a test tube type quart glass sleeve of 4 cm diameter, inside the quarts tube rested a Mercury UV (4/120SE) from Applied UV cc (South Africa). The reactor system was situated in a completely dark room with a controlled temperature in the ambient range.

3.12.1 Reactor temperature cooling

It has been documented that photocatalytic reactions are influenced by temperature (Pang et al., 2009; Perez et al., 0000; Andreozzi et al., 1999; Hoffmann et al., 1995; Fox and Dulay, 1993; Chemseddine and Boehm, 1990). To determine that the reactor experiment solution temperatures did not elevate beyond the desired range. A pseudo-experimental setup was conducted under the designed experimental conditions.

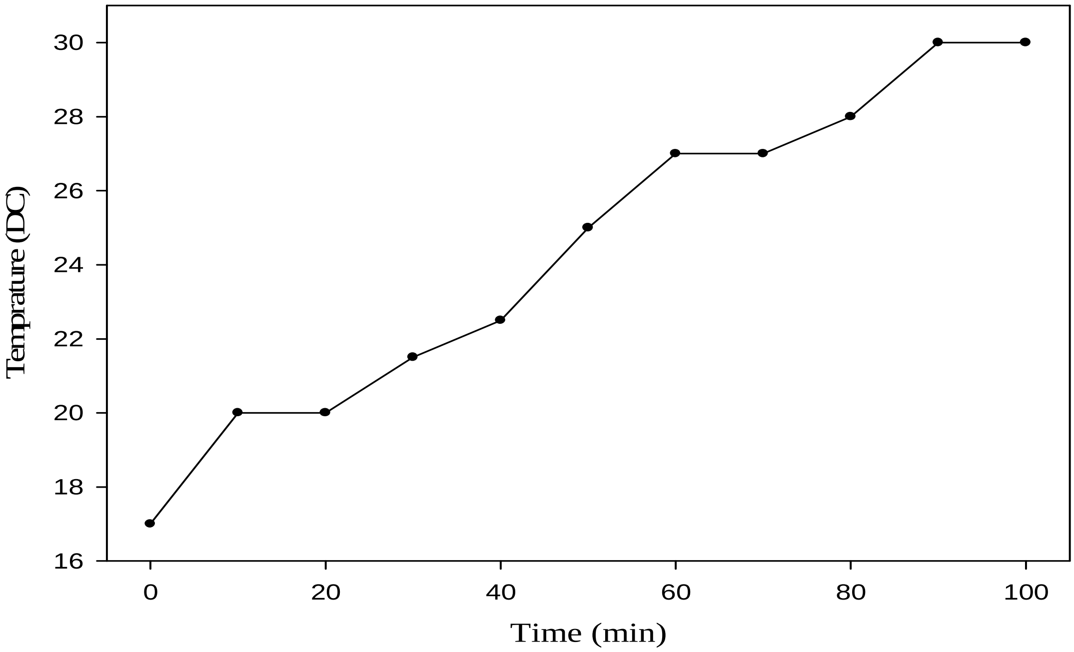


Figure 3.2: Reactor temperature vs. time elapse

An ice bucket of 12 L of tap water and 8 L of ice was prepared and pump driven into the jacketed glass beaker. The temperature was measured at determined time intervals using a mercury thermometer. The settled ice bucket temperature was measure at 8˚C. Figurative representation of the reactor measured temperatures over time is represented in Fig.3.2. The initial reactor solution temperature was measured at 17˚C, there was a slow and gradual increase in temperature over a 100 minute period up to 30˚C. The experimental procedure in this study is designed to run for less than 60 minutes. The resulting measurements represented in Fig.3.2 suggest that reactor temperatures were unlikely to exceed 30˚C, which is in the ambient temperature range, thus attributing degradation mainly due to UV radiation.

CHAPTER 4: ENVIRONMENTAL DISTRIBUTION

4.1 Introduction

Organochlorinated compounds enter the environment mainly through the use of pharmaceuticals in agriculture and industrial productions. Developing countries are documented to have the highest growth and usage of these compounds (Rantane et al., 1986). This situation is exacerbated by the continuous revolutionising of technologies to produce new and more effective chemicals (Bolong et al., 2009). The manufacture and illegal disposal of magnitudes of industrial chemicals and unregulated occupational exposure contribute to a significant amount of environmental pollution in urban South Africa (Bornman et al., 2007) whereas agricultural application is the major contributor of organochlorinated endocrine disrupting chemicals in the rural demarcations of the country. Studies by Bornman et al., (2007), Slabbert et al., (2007a, b) documented significant amounts of estrogenic activity in surface waters. These findings are evident in spite of the existence of regulations of pesticides imports in the past three decades in South Africa (Philogene, 1985).

In this study the states of EDCs and OCPs of concern is mitigated for the immediate South African environment. A comparative analysis of environmental incidence against allowable levels in local and international standards will be conducted.

4.2 Water properties

Table 4.1 presents water properties and the concentration of dissolved solids in water prior to analysis. From sample observation upon collection, water samples from dams 1 and 3 contained suspended matter of algal nature, elucidated by a green colour. This can be assumed to result from the eutrophication proceeding heavy rain falls, as these water sources are renowned to poses eutrophic properties resulting from the mineral influx of the feeding rivers. Knowing the water properties of the samples assisted in normalising the sample extraction process as pH and conductivity would affect the reproducibility of a standard matrix amongst samples. Instrumental analysis generally takes into account the subtraction of matrix background. In some cases in the analysis, the recorded matrix values were high enough to have significant impact on the results interpretation when subtracted, and therefore all recorded values in all the determinations did not take into account background elimination which varied significantly from one sample to the next.

Table 4.1: Physical properties of the water from WWTP and dams

Sample Identity	Conductivity (µS)	Salinity (%)	TDS (mg/L)	pH
A1	1702	0.8	812	6.72
A2	1020	0.5	482	7.23
A3	1047	0.5	492	7.02
B1	1962	1.0	940	6.59
B2	1168	0.6	554	6.88
B3	1203	0.6	569	7.20
C1	2017	1.1	1050	6.83
C2	1580	0.8	760	6.65
C3	1205	0.6	573	6.56
DAM 1	1231	0.6	600	7.68
DAM 2	684	0.3	330	9.91
DAM 3	1061	0.5	496	9.04

TDS – Total Dissolved Solids

4.2.1 Analysis of OC compounds

Fig.4.1 represents the concentrations of the analyte compounds and the relative abundance of organochlorinated pollutants in water samples from the designated sampling locations. Water from wastewater sites were collected whilst in continuous flow. Due to this nature of this form of sampling, the acquired samples are likely to exist as discrete flows in the respective flow-mass, not necessarily reflecting the concentrations of a total volume. The relatively high values acquired may be misled by this phenomenon, as it can be argued that significantly different results may be acquired from the same sampling point with the slightest difference in the timing of sampling. Dam water samples may thus be a better reflection of settled water pollutant concentrations. Results do indicate that the dam samples recorded a more consistent range of values oppose to the WWTP samples which depicted significant variable range in samples from the same location.

A liquid/liquid extraction method is generally recommended as is stated to more accurate, but due to its large (1000 mL) required sample, SPE was preferred due to circumstances beyond control. The extraction method has the potential for analytical error in terms of the recovery from different samples.

4.2.1.1Wastewater treatment plants

Table 4.2 shows the concentrations of the pollutant compounds from the different sampled sites. WWTP A organochloride pollutant concentration levels range from 2 ng/L (PCB 25) to 90 ng/L (Chlordane). Wastewater treatment plant B recorded concentration levels ranging from 1 ng/L (PCB 25) to 301 ng/L, while plant C ranged from 4 ng/L (DDE, DDT) to 251 ng/L (Chlordane). WWTP A depicts lower values for most of the selected compounds. This situation is to be expected given the location of the treatment plant and the type of influent received. WWTP A is located alongside a central business district, receives influent comprising mainly of the domestic waste and limited industrial waste. The organochloride pesticides concentrations recorded from this location could be mainly attributed to private home-based applications, which include: (i) landscaping companies servicing commercial and residential customers, they generally use pesticides to maintain lawns and gardens in recreational parks; (ii) and home owners, who frequently use commercially available products to maintain their lawns and gardens.

The concentration values recorded in treatment plants B and C can be paralleled for most results. This is expected as these facilities are located in the same demarcation, less than 5 km apart. The surrounding environment consists mainly of agricultural farmlands and livestock, scattered households, and vast veldts. The organochloride pesticide concentrations recorded in treatment B and C are relatively high, this correlates with the direct nature of pesticide application to agriculture and farmlands. It can be speculated that during the period prior to sanctioning of pesticides in the country, there was significant application of these agrochemicals, which may still be embedded in agricultural field soils and beyond.

Table 4.2: Recorded concentrations (ng/L) of each compound from each treatment plant

Sample	2.3.4-Trichlorobiphenyl	Heptachlor	Chlordane	DDE	DDT
A1	5	34	90	5	4
A2	8	17	36	4	3
A3	2	13	47	5	9
B1	6	34	164	9	7
B2	1	51	301	15	22
B3	8	18	119	13	19
C1	9	16	133	7	9
C2	11	52	251	5	56
C3	5	28	152	4	4
D1	6	37	94	21	28
D2	1	22	50	24	17
D3	5	36	70	8	9

4.2.1.2Dams

The analyte compound concentration levels in the dams ranged from 1 ng/L (PCB 25) to 94 ng/L (Chlordane). The recorded values are generally lower than those recorded at the wastewater treatment plants. Dam 1 recorded higher concentrations of the contaminants than dams 2 and 3, this is expected given the location of the dam and the nature of inflowing pollution. Dam 1 is situated in a mountainous region alongside agricultural harvest, receives domestic and industrial effluent of long range transportation carried by the Crocodile and Magalies Rivers. The dam is larger in size and harbours pollutants from most of the Gauteng region. Dam 2 recorded concentration levels ranging from 1 ng/L (PCB 25) to 50 ng/L (Chlordane), while dam 3 ranged from 5 ng/L (PCB 25) to 70 ng/L (Chlordane). As stated previously, dams 2 and 3 recorded lesser concentrations in comparison to dam 1, this should hold true given that the dams do not poses pollution sources of the same magnitude. Dam 2 mainly receives effluent from wastewater treatment plants B and C, and the Pienaars River, which does not carry significant pollution. Dam 3 is located inside a nature reserve within city limits, and has no direct sources of pesticide pollutants apart from local domestic and industrial applications.

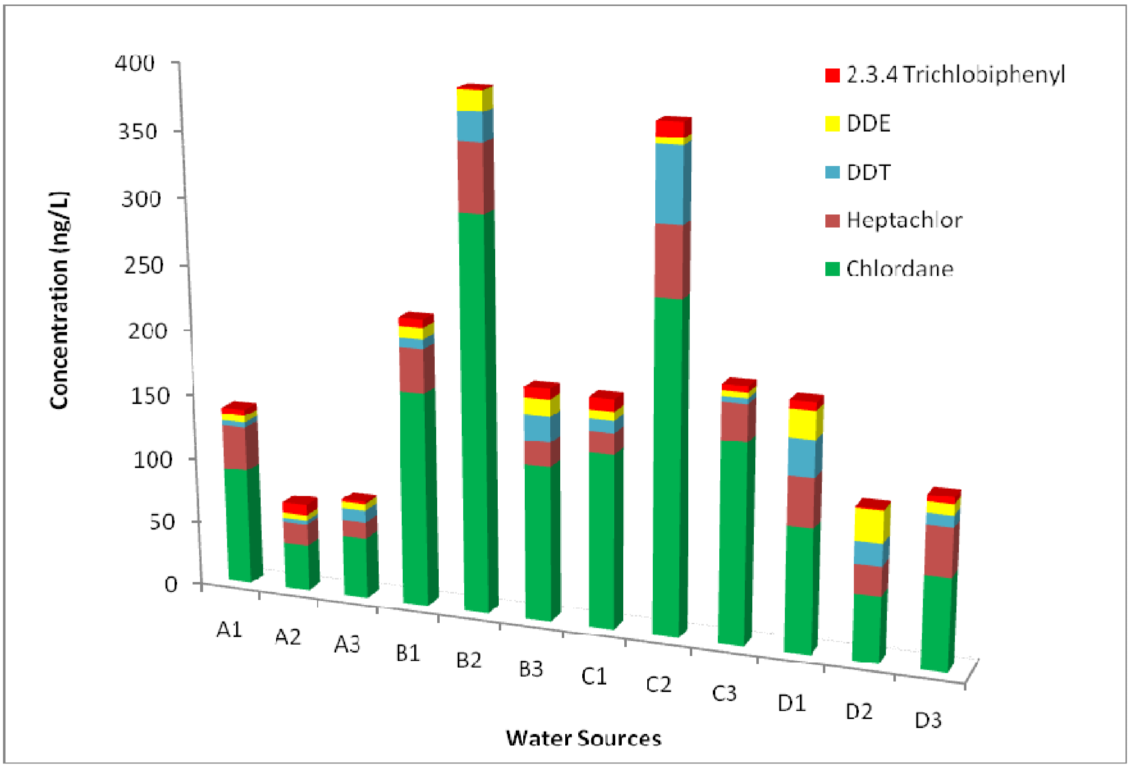


Figure 4.1: Identified organochloride compounds detected in the environmental water and the relative abundance

4.2.1.3Assessment of organochloride chemicals

Polychlorinated biphenyls are generally used as additives to oils in electrical equipment, hydraulic machinery, and in chemical stabilisation (UNEP, 1999). 2.3.4-Trichlorobiphel was recorded ranging from 1 ng/L (B2, D2) to 11 ng/L (C2), the concentrations are not alarming in comparison to the other organic compounds analysed. The chlorobiphenyl concentrations recorded were relatively consistent in all the sampling locations (less than 8 ng/L average), even though treatment plant C recorded slightly higher results. The study regional location is not industrialised, especially in the field of hydraulic machinery and dielectrics production. Chlorinated biphenyls are thus not expected to be prominent in the region.

Heptachlor concentrations ranged from 13 ng/L (A3) to 52 ng/L(C2). Treatment plant A averaged 21 ng/L, while plant B and C averaged 34 and 32 ng/L, and the dams recorded an average of 32 ng/L heptachlor concentrations respectively. Chlordane recorded relatively higher concentrations in comparison to the rest of the organic analyte compounds, ranging from 36 ng/L (A2) to 301 ng/L (B2). Wastewater treatment plants averaged 144 ng/L of chlordane, while the dams recorded an average of 71 ng/L.

DDE concentrations in water ranged from 4 ng/L (A2, C3) to 24 ng/L (D2). WWTP A and C averaged 5 ng/L, while plant B averaged 12 ng/L DDE. The Dams DDE concentrations averaged 18 ng/L, a bit higher than the wastewater samples. DDT concentrations in water ranged from 3 ng/L (A2) to 56 ng/L (C2). WWTP A recorded the lesser concentrations of DDT, correlating to limited urban pesticides application.

4.2.1.4 Assessment of compounds by source

Fig.4.2 represents the 3 most abundant organochloride (DDT, Heptachlor, and Chlordane) in the region from the designated sources. Taking into account that each WWTP has 3 independent sampling points, it is expected that there will significant variation within each plant. This is because the system is continuous flow and there is no direct relation between the pollutants and the pollutant source. It is expected that there would be an indirect relationship of the magnitude of pollution entering the facility depending on the location and the type of organic discharge expected. WWTP A is located in an urban location, therefore it would be expected that most sampling points will depict recording lower than those expected from the agricultural location, where WWTP B and C are found. Table 4.3 shows the highest concentration levels from each location for DDT, Heptachlor and Chlordane.

It is evident from Table 4.3 that WWTP A has the lowest recording of the pesticide compounds in comparison to the other location as was expected. With the exception of the DDT highest concentration at location C, the rest of the recorded values are in agreement that the pesticide concentrations from locations B and C are similar. This is expected as both the location depicts similar habitation and usage.

The results of the dam samples shown in Table 4.4 are somewhat in agreement with the principle given above. Given the location of dam 1, this is in a mountainous area surrounded by agricultural farmlands. It is expected that the pesticide concentration would be higher than the other 2 locations.

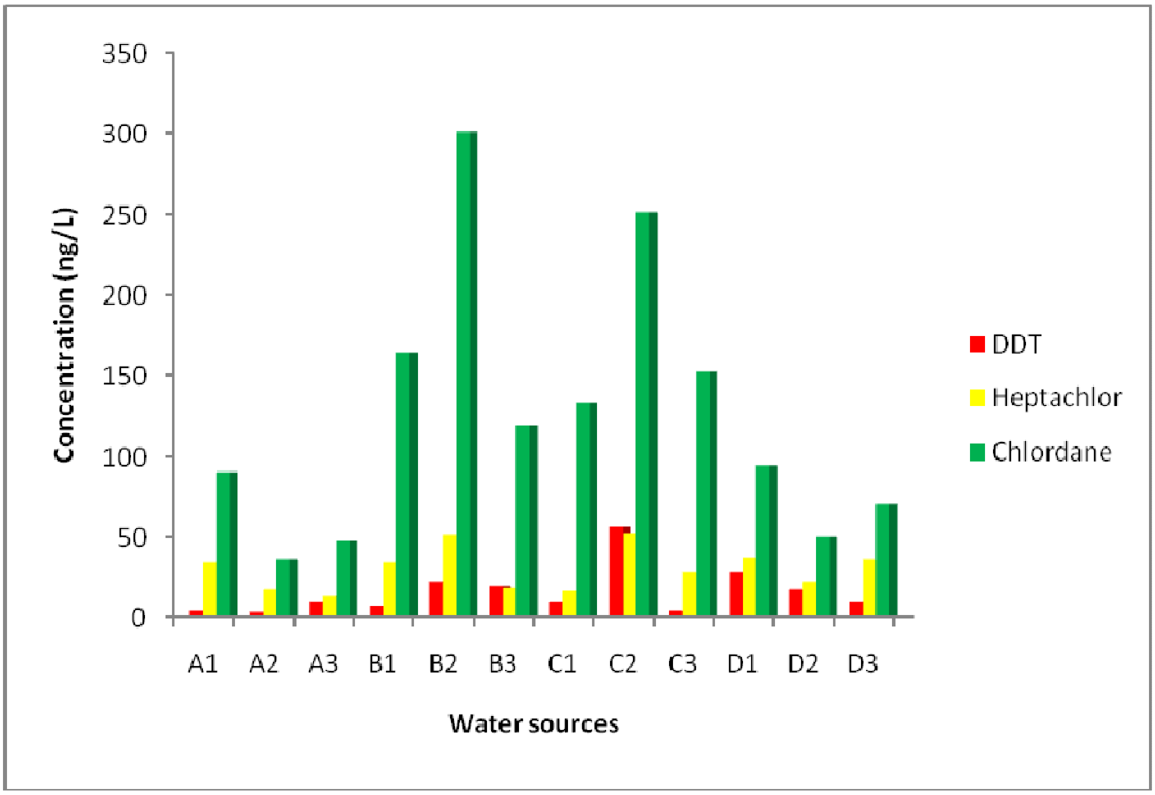


Figure 4.2: Most abundant organochlorides from the sources

Table 4.3: Highest recorded concentrations (ng/L) of each compound from each plant

Compound	WWTP A	WWTP B	WWTP C
DDT	9	22	56
Heptachlor	34	51	52
Chlordane	90	301	251

Table 4.4: Recorded concentrations (ng/L) of each compound from the dams

Compound	DAM 1	DAM 2	DAM 3
DDT	28	17	9
Heptachlor	37	22	36
Chlordane	94	50	70

4.2.1.5Water quality standards

The South African water quality guidelines to protect aquatic ecosystems are shown in Table 4.5. DDE is not specified, but can be assumed to be parallel to DDT as the parent compound. Polychlorinated biphenyls do not have a specified limit, but it is documented in the guidelines that any detected PCB must be considered serious (DWAF, 1996). Above these specified concentration limits, the fitness of species in the aquatic systems in terms of health, reproduction and behaviour is effected (DWAF, 1996).

The study findings suggests that all the compounds detected from all the sampling sources are much higher than the specified in the South African guidelines documented limits. The values are alarming in comparison.

Table 4.5: Water quality standard concentrations (ng/L) in aquatic systems

Compound	S.A Guidelines
DDT	1.5
Heptachlor	5
Chlordane	25
PCBs	Not specified
DDE	Not Specified

Even though the study values were probably elevated by the accumulated compounds due to significant rainfalls, the figures are a reflection of the chemicals embedded in soil and sediment, and circulating in the aquatic environment. Considering that any detection of PCB should be regarded as serious, concentration levels reading 11 ng/L are far too high to be disregarded. Heptachlor and chlordane in some samples are ten times higher than the regulated concentration limits. Sample C2 recorded a DDT concentration of 56 ng/L, which is astounding in comparison to the 1.5 ng/L specified by the guidelines. The presence of organochlorinated compounds at the concentrations detected in this study is a cause for concern. The health implications of rural communities who are direct users of water from dams and wildlife are significant. This situation is exacerbated by the inability of wastewater treatment facilities in removing the types of pollutants, which means that these compounds are continuously accumulated in aqueous systems.

CHAPTER 5: DEGRADATION RESULTS

5.1 Photocatalysis mechanism

The schematic diagram represented in Fig.5.1 is the heterogeneous photocatalysis mechanism using titanium dioxide proposed by Mills and Le Hunte, (1997) and Hoffmann et al., (1995). Each of the primary steps is described briefly using the generated equations correlating to Fig.5.1. The first equation (5.1) represents the charge-carrier generation upon the illumination of the semiconductor, this reaction if very fast and generates the conductive band electron (e_{bc}^{-}) resulting in the valence band positive hole (h_{bv}^{+}).

$$TiO_2 + hv \rightarrow h_{bv}^{+} + e_{bc}^{-} \tag{5.1}$$

The primary process following Eq.5.1 is charge-carrier trapping, resulting in the reduction of titanium. Eqs.5.2 and 5.3 are also fast reactions, resulting in the trapping of the valence band positive holes ($Ti^{IV}OH^{\circ+}$) and conduction band electrons ($Ti^{III}OH$), where $Ti^{IV}OH$ represents the primary hydrated titanol group.

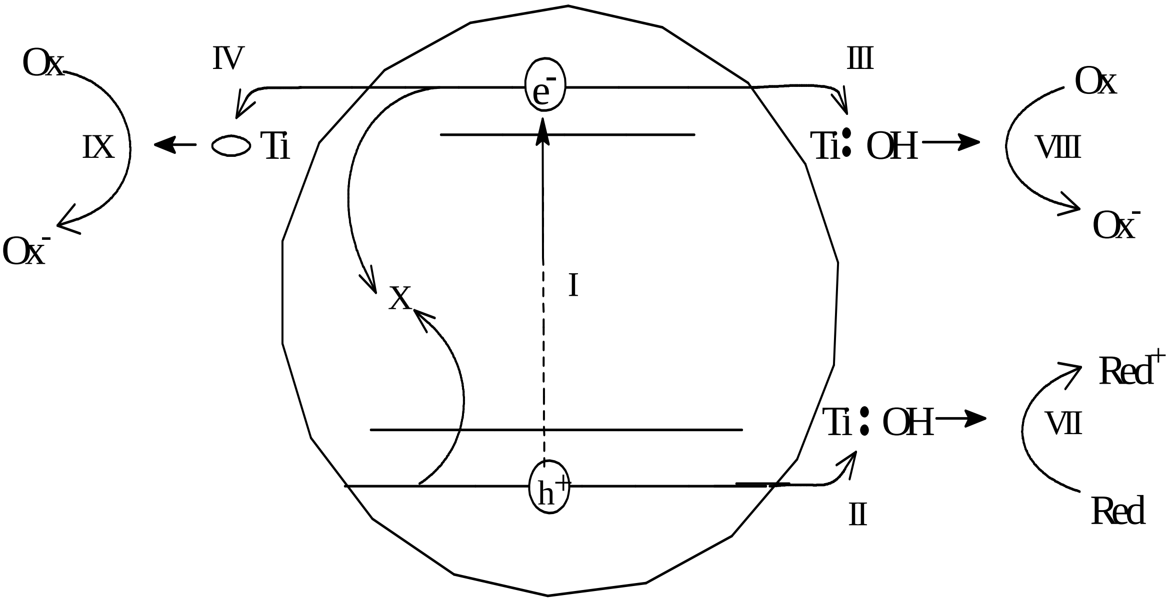


Figure 5.1: Schematic diagram of the primary steps in the photocatalytic mechanism

$$h_{bv}^{+} + Ti^{IV}OH \rightarrow Ti^{IV}OH^{\circ+} \tag{5.2}$$

$$e_{bc}^{-} + Ti^{IV}OH \leftrightarrow Ti^{III}OH \tag{5.3}$$

Eq.5.4 explains the conduction band electron being somewhat trapped on the surface of the oxide, this is a fast irreversible process producing a Ti^{III} ion.

$$e_{bc}^{-} + Ti^{IV} \rightarrow Ti^{III} \tag{5.4}$$

Following charge-carrier trapping process, is charge-carrier recombination of the valence band electron and the conduction band hole. Eq.5.5 is a relatively slow process taking 100 x 10^{-9} s, while Eq.5.6 is a fast (10 x10^{-9} s) reaction.

$$e_{bc}^{-} + Ti^{IV}OH^{\circ+} \rightarrow Ti^{IV}OH \tag{5.5}$$

$$h_{bv}^{+} + Ti^{III}OH \rightarrow Ti^{IV}OH \tag{5.6}$$

Interfacial charge transfer is the next primary process step, in this step reduction-oxidation reactions take place between the reducing agents and the oxidising agents. In Eq.5.7 the trapped valence band positive hole (Ti^{IV}OH$^{\circ+}$) is reduced using molecular oxygen, where *Red* represents the electron donor. This is a slow reaction, taking 100 x10^{-9} s.

$$Ti^{IV}OH^{\circ+} + Red \rightarrow Ti^{IV}OH + Red^{\circ+} \tag{5.7}$$

In Eq.5.8, the conduction band electron (Ti^{III}OH) is oxidised by an organic compound, where *Ox* represents the electron acceptor, this is a very slow process.

$$Ti^{III}OH + Ox \rightarrow Ti^{IV}OH + Ox^{\circ+} \tag{5.8}$$

The semiconductor composition is reduced back to its initial configuration. This takes place in Eq.5.9 where an oxidising agent is used to retain the initial valence state of Ti^{IV}.

$$Ti^{III} + Ox \rightarrow Ti^{IV} + Ox^{\circ+} \tag{5.9}$$

It should be noted that trapped electrons and surface positive holes can undergo a very quick recombination reaction. Eq.5.10 depicts this process ranging at times of 10^{-12} seconds.

$$h_{bv}^{+} + e_{bc}^{-} \rightarrow hv \qquad (5.10)$$

Competition between charge carrier recombination processes and interfacial charge transfer processes determines the rate of the overall reaction. Inhibition of the recombination processes may increase the rate of interfacial charge transfer. The mechanism represented in Fig.5.1 does not take into account the organic molecules reacting directly with the charged surface hole, it assumes that the hydroxyl (OH°) radical is the only route taken. Serpone (1995), Pelizzetti and Minero (1993), and Terzian et al., (1991) propose additional routes to the hydroxyl radical formation.

5.2 Degradation of organochloride compounds

The principles of photocatalysis are applicable to many organic compounds. Bhatkhande et al., (2001) suggest that almost all organic and inorganic substances can be degraded using photocatalysis. Compounds targeted in this study are organochlorinated pesticides (Heptachlor, Chlordane, DDE, and DDT) and a polychlorinated biphenyl (2.3.4-Trichlorobiphenyl). Pesticides and PCBs are by nature toxic to all living organisms, and the end users of contaminated waters are in danger of endocrine system dysfunctions. Current wastewater technologies are inefficient at removing most endocrine disrupting chemicals. There is therefore a great need for the development of techniques and processes to deal with this problem. Some wastewater treatment plants use UV radiation (photolysis) and chlorination for treatment and disinfection of wastewater.

In application, there have been documented challenges against TiO_2 photocatalysis in water treatment, they are: (1) the difficulty in recovering the fine semiconductor particles from solutions; (2) the rapid charge carrier recombination reaction in comparison to the oxidation reduction reactions resulting in low quantum yield; and (3) the inability to use solar energy resulting from the high band gap energy required (Chiang et al., 2002). When natural sunlight is used for the process, only about five percent of the radiation has sufficient energy to complete the process (Wilke and Breuer, 1999). A proposed and documented solution to overcome this challenge has been to dope titanium with transition metal ions.

Many transitional metal ion dopants with improved rates of photocatalytic oxidation reactions have been found that act by modifying the electron-hole recombination and interfacial charge transfer processes (Chiang et al., 2002; Wilke and Breuer, 1999; Sykota, 1997; Choi et al., 1994). Changes in reaction rates have been demonstrated by trapping the electron and hole with metals ions (M^{n+}), by Chiang et al., (2002) and Choi et al., (1994), following the process elucidated in the photocatalytic reaction Eqs 5.11 and 5.12 derived by Mills and Le Hunte, (1997) and Hoffmann et al., (1995).

$$M^{n+} + e_{bc}^{-} \rightarrow M^{(n-1)+} \tag{5.11}$$

$$M^{n+} + h_{bv}^{+} \rightarrow M^{(n-1)+} \tag{5.12}$$

Transitional metal ions frequently used are Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}, V^{4+}, Mo^{5+}, Pb^{2+}, and Tl^{+} (Chiang et al., 2002; Wilke and Breuer, 1999; Sykota, 1997; Choi et al., 1994). Copper oxide has been investigated widely and documented to have profound influence in heterogeneous photocatalysis of organic compounds in aqueous solutions.

Photocatalytic degradation studies are still at lab-scale experimentation levels, unlike some advanced oxidation processes (AOP) which have reached commercialisation. This study will attempt to investigate the: (i) feasibility of treatment applying heterogeneous photocatalysis principles in comparison to conventional photolysis; (ii) investigate the semiconductor (TiO_2) efficiency in the oxidative degradation of organochlorinated compounds in water solutions; and (iii) investigate the use of copper oxide (Cu^{2+}) as a dopant in an attempt to improve the efficiency of the photocatalytic oxidation of organochloride compounds. The investigation will be conducted by applying radiation to a semiconductor catalyst suspended in an organochlorinated spiked water solution. Reverse phase solid phase extraction (SPE) will be used in preparation of the analytical samples, and GCMS will be used for analysis. The optimum concentration and efficiency of the catalysts will be determined from various experiments for individual chemicals of interest.

5.3 Degradation with undoped catalyst

The mineralisation of DDT, DDE, Heptachlor, Chlordane, and 2.3.4-Trichlorobiphenyl under UV radiation in the presence of a TiO_2 semiconductor suspended in aqueous solutions at ambient temperatures was investigated in this study. Different concentrations of the catalyst were prepared in aqueous solutions to determine the optimum catalyst degradation concentration of each organochlorinated compound under investigation. Results of each of the chemical compounds under study will be presented and discussed briefly. It is important to note that some figure representations on the treated chemicals reach a near zero state of removal without reaching the 0 barrier concentration, in most cases this is due to high matrix (background) responses. In some cases the matrix values were high enough to have significant impact on the results interpretation when subtracted, and therefore all recorded values in all the experiments did not take into account background elimination which varied significantly from one sample to the next.

5.3.1 Degradation kinetics

In the investigations conducted in this study project, one parameter was varied and all others were assumed to be kept constant through-out, neglecting the possible compound to compound interactions of the analytes of interest and their competition for available activated catalyst surface sites. The temperature was maintained at a range assumed not to interfere with the investigation. The general rate degradation expression of $r = - kC$ was used to predict rates of reactions for all the given organochloride compounds, where C depicts the analyte compound. Some literature has reported that zero and first order reaction kinetics being adequate at modelling the photocatalysis of organic compounds at low chemical analyte concentrations. This was anticipated to be applicable in this study as the range of analyte compound concentrations was targeted to be less or equal to 100 ng/L. In most kinetic experiments, the oxidation kinetics generally depicts an increase in the degradation rates of the compound over time until it reaches a zero rate. This fits the generally accepted Langmulr-Hinshelwood (L-H) kinetics model in Eq.5.13, where k_r is the reaction rate constant, C is the concentration of the organic analyte compounds, and K is the Langmulr adsorption constant. The model assumes that the: (1) the model is at equilibrium, the number of surface adsorption sites is fixed; (2) only one substrate may bind at each surface site; (3) the rate of adsorption by the substrate is identical for each site and is independent of surface coverage; (4) there is no interaction between adjacent adsorbed molecules; (5) the rate of surface adsorption of the substrate is greater than the rate of any subsequent chemical reactions; and (6) no irreversible blocking of active sites by binding to product occurs (Fox and Dulay, 1993).

$$r = dC/dt = k_r KC/[1 + KC] \tag{5.13}$$

The *K* value represents the catalyst adsorption capacity, and can be solved for *t* using discrete changes of concentration (C_t) from the initial concentration (C_i).

$$\ln(C_t/C_i) + K(C_t - C_i) = k_r Kt \tag{5.14}$$

The *K*-value can be calculated using a linearised representation of Eq.5.13, where 1/*r* is plotted against 1/*C*.

$$1/r = 1/ k_r KC \tag{5.15}$$

The *K*-value obtained from the linearised plot will be significantly smaller than the initial value. This is generally achieved when the organic analyte compounds concentrations are low, thus giving a first order reaction expression evident in Eq.5.16.

$$r = dC/dt = k_r KC = kC \tag{5.16}$$

Rearranging Eq.5.16 produces a first order model, as represented in Eqs.5.17 and 5.18.

$$C = C_i\, e^{-kt} \tag{5.17}$$
$$\ln(C_i/C_t) = -k_r Kt = -\, kt \tag{5.18}$$

The parameter under investigation in this project was the catalyst concentration (C_c), and the efficiency of oxidation of the analysed chemicals. The rate expression required modification to elucidate the rate constant as a function of the catalyst concentration $k = f(C_c)$ as the chemical compound concentration were not varied. The surface characteristics of the semiconductor in question were assumed not to be affected by the solution matrix. Studies have declared illumination hindrance due to opacity and light scattering and thus decrease in the passage of irradiation through the solution as a factor that can introduce experimental error from excessive photocatalyst application (Pang et al., 2009; Dox and Dulay, 1993; Ollis et al., 1991), but models have been developed to identify optimum catalyst concentrations. This study will only take into account catalyst application as the varied parameter, and simulated data will be used to estimate the rate constant values to determine reaction kinetics.

5.3.2Kinetic model for oxidation of organochloride compounds

Four catalyst concentration were used to investigate the oxidation kinetics of the organochloride compounds (C_c = 5, 10, 30, 50, and 200 mg/L). These will be used to establish the relationship between rate constant (k) and catalyst (C_c). On condition that the batch reactor is mixed completely, the power of the lamp is maintained, and the UV intensity is kept constant, only one factor is related to k: the photocatalyst concentration (Pang et al., 2009, Daneshvar et al., 2004). As indicated earlier, k is a function of the C_c, and the generated rate expression is represented in Eq.5.19.

$$r = kf(C_c).C. \qquad (5.19)$$

5.3.2.1 DDT

The heterogeneous photocatalysed oxidation of DDT in the presence of the titanium dioxide semiconductor and in the absence of the semiconductor is presented in Fig.5.2. A detailed analysis of the kinetics is explained in section 5.3.2.1. To investigate the degradation efficiency of the titanium oxide catalyst, analysis of catalyst concentrations of 0, 5, 10, 30, 50, and 200 mg/L were conducted. It is evident from Fig.5.2 that photocatalysis using 5 mg/L TiO_2 concentration has a more favoured degradation rate than the other concentrations. Fig.5.2 suggests that DDT removal efficiency deteriorates with increased catalyst concentration above the 5 mg/L catalyst concentration. The 10 minute point clearly elucidates the correlation of removal and catalyst concentration, at this point nearly 93 % of DDT is removed using the 5 mg/L concentration, while 82 %, 75 %, 67%, 24% were removed using the 10, 30, 50, and 200 mg/L respectively. It is also interesting to note that at the 10 minute point nearly 82 % of DDT had been degraded in the photolysis experiment, this suggested that photocatalysis at catalyst concentration above the 5 mg/L maybe even less favourable than without the application of the catalyst.

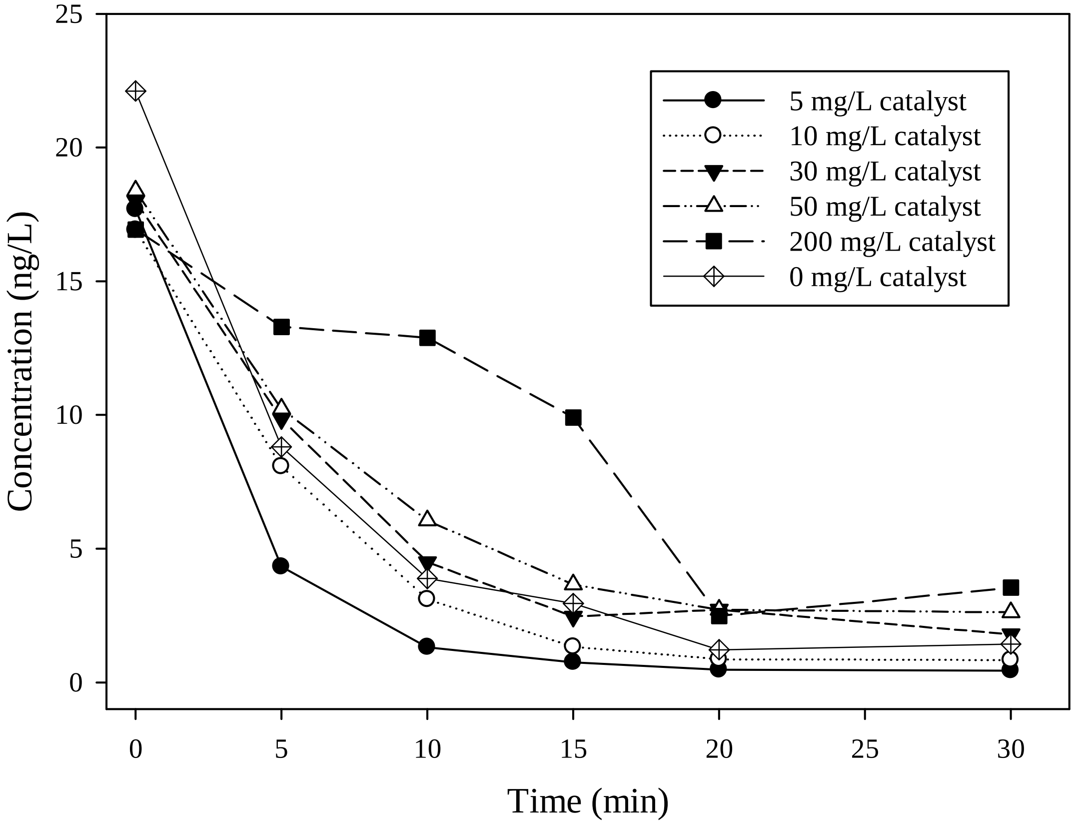


Figure 5.2: DDT photocatalytic degradation in aqueous solutions in the presence of different concentrations of anatase TiO_2, 20 ng/L DDT.

From Fig.5.2 it can be anticipated that complete removal by the 5 mg/L concentration is achieved in less than 15 minutes. It can be assumed that beyond titanium dioxide concentrations of 200 mg/L, catalyst degradation creeps near the saturation point.

5.3.2.1.1 Evaluating the model of DDT degradation

The rate of DDT degradation and the relationship with the catalyst concentration is given in Eq.5.19. The degradation constants of DDT in different catalyst concentrations are shown in Table 5.1. The effect of *k* for DDT degradation can be linearised using an inverse of the catalyst concentration ($1/C_c$). It is evident from Table 5.1 that the degradation constant is decreased with increasing catalyst concentration.

Table 5.1: Simulated degradation constants for DDT oxidation

Catalyst concentration (C_c) (mg/L)	Degradation constant (k)
0	0.1551
5	0.2646
10	0.1615
30	0.1189
50	0.0984
200	0.0680

Mean = 0.1444 Std dev = 0.06849

Fig.5.3.A represents the simulated degradation of DDT using different catalyst concentrations, depicts the relation between catalyst concentration and the degradation rate. The degradation constant is decreased with increasing catalyst concentration with a mathematical equation of:

$$k = 0.894(1/C_c) + 0.081 \; (r^2 = 0.99) \qquad (5.20)$$

With the k value calculated, the reaction model can be determined using parameter estimated simulated results. Fig.5.3.B shows the linear correlation between –ln (C_t/C_i) and time, where C_t represents the concentration over time and C_i is the initial concentration. The oxidation of DDT is represented adequately by the first order kinetics:

$$r = dC/dt = - kC \qquad (5.21)$$

Fig5.3.A essentially shows that the degradation rate of DDT was not linear with respect to the concentration of the semiconductor catalyst, as less DDT was removed with increased catalyst loading, k is therefore expressed as indicated in Eq.5.20. Based on the above model, the rate of DDT oxidation can be expressed as indicated in Eq.5.22.

$$r = dC/dt = - 0.894(1/C_c) + 0.081 \times C \qquad (5.22)$$

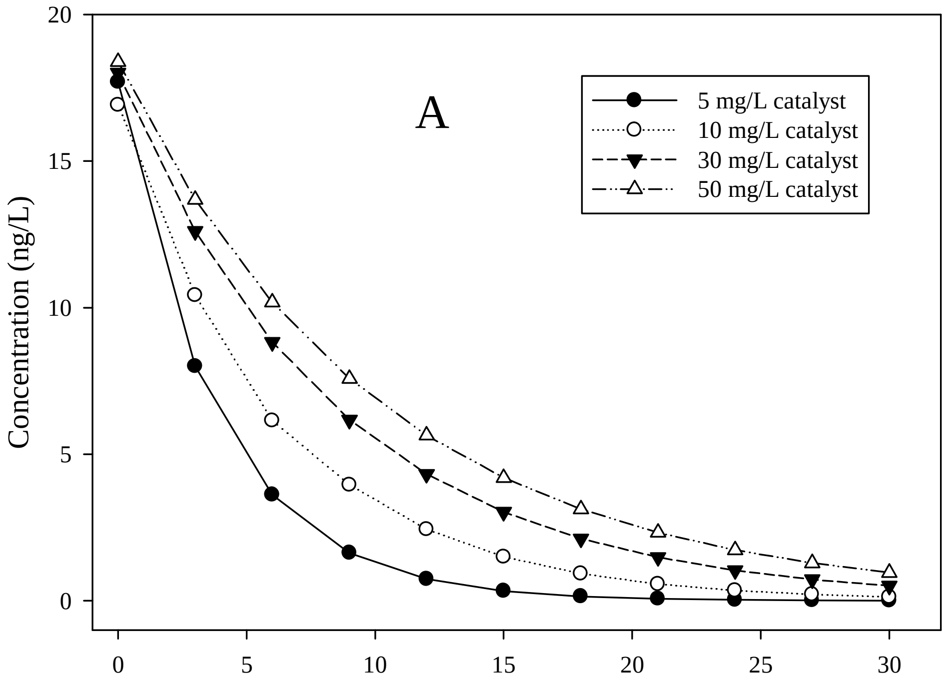


Figure 5.3A: Simulated DDT photocatalysis versus time using TiO_2 catalysis at different concentrations.

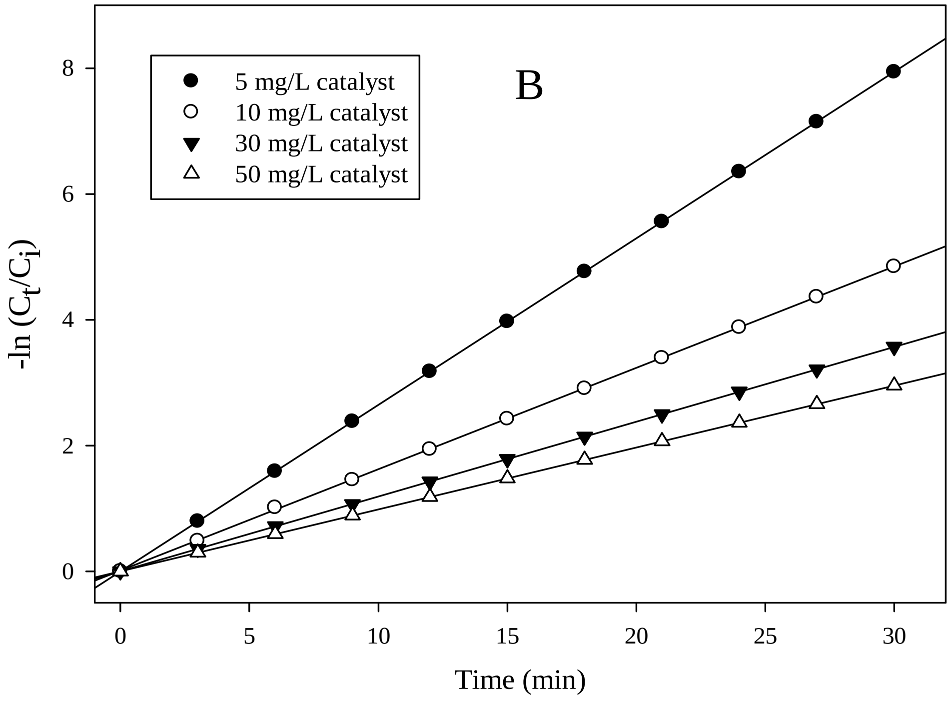


Figure 5.3B: First order rate profiles of DDT photocatalysis using TiO_2 catalyst.

5.3.2.2 DDE

The heterogeneous photocatalysed oxidation of DDE in the presence of the titanium dioxide semiconductor and in the absence of the semiconductor is presented in Fig.5.4. From this figure, it can be observed that most of the degradation takes place within the first 5 minutes of solutions irradiation. From this data, it cannot be concluded whether photocatalysis has an improved performance on photolysis. Fig.5.4 represents the degradation of DDE with increasing catalyst concentrations.

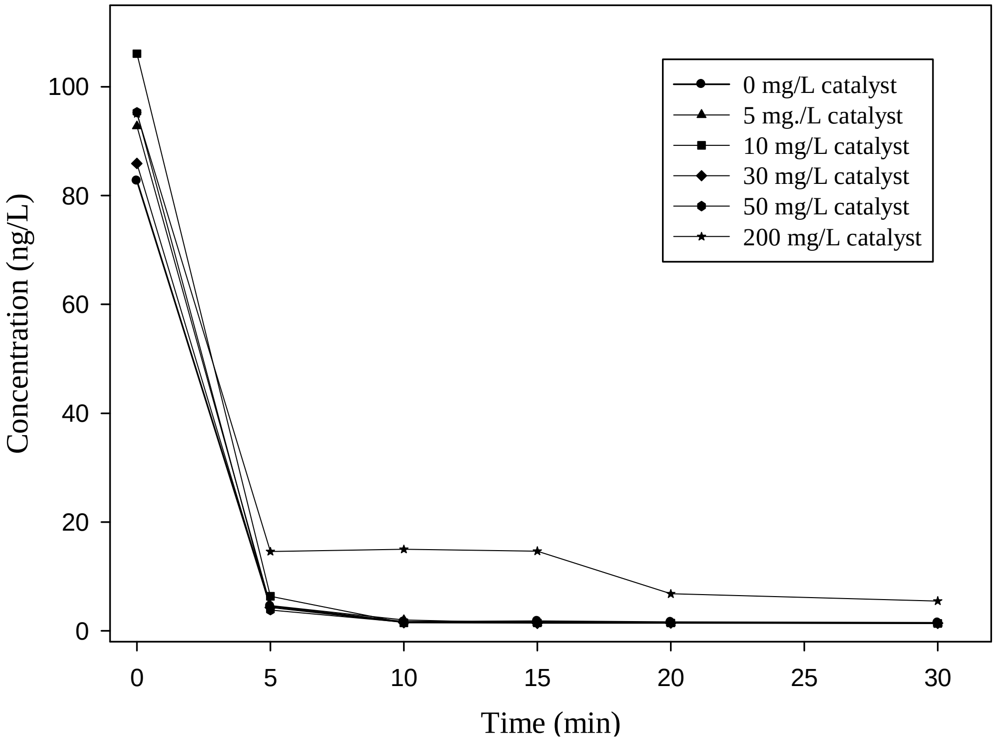


Figure 5.4: DDE photocatalytic degradation in aqueous solutions in the presence of different concentrations of anatase TiO_2, 100 ng/L DDT.

It would have been insightful to conduct a minute to minute study of DDE under these conditions for the period prior to 5 minutes, where it could be conclusively determined whether catalyst application improves mineralisation, but due to the relatively increased anticipated error in sampling at the shorter sampling intervals (the sampling procedure took approximately 30 seconds, which included submerging the sampling tube; drawing of sample; emerging the tube; and transfer into extraction cartridge), the effort would have not been feasible, and the conclusive nature of the results would be questionable. To confirm the non conclusive nature of the data, a simulated model of degradation was conducted. Table 5.2 shows the degradation constants of DDE for each catalyst concentration. Simple statistics show that only the 200 mg/L catalyst concentration degradation constant is beyond the standard deviation to the average value.

Table 5.2: Simulated degradation constants for DDE oxidation

Catalyst concentration (C_c) (mg/L)	Degradation constant (k)
0	0.5638
5	0.5814
10	0.5443
30	0.5826
50	0.6310
200	0.2808

Mean = 0.5307   Std dev = 0.1257

5.3.2.3 Heptachlor

The heterogeneous photocatalysed oxidation of heptachlor in the presence of the titanium dioxide semiconductor and in the absence of the semiconductor is presented in Fig.5.5. The overall degradation of heptachlor using the 5 mg/L catalyst mediated photo degradation depicts slightly more favourable results, better than photolytic degradation under the same conditions. There is an observed decrease in catalytic efficiency with increased catalyst concentration, this observation is best represented at the interval between 5 and 10 minutes of Fig.5.5, where 76 %, 67%, 62%, 51%, and 35% were recorded by the 5, 10, 30, 50, and 200 mg/L catalyst concentrations respectively. Near complete degradation of the heptachlor by the 5 mg/L catalyst appears to occur proceeding 15 minutes of irradiation. With the exception of the 200 mg/L catalyst concentration experiment, the other catalyst experiments reached near complete degradation of heptachlor within the 30 minute period.

5.3.2.3.1 Evaluating the model of heptachlor degradation

The rate of heptachlor degradation and the relationship with the catalyst concentration is also represented by Eq.5.19. The degradation constants of heptachlor in different catalyst concentrations are shown in Table 5.2. From the standard deviation, it is evident that there is a significant difference between the photocatalysis and photolysis experimental degradation of heptachlor.

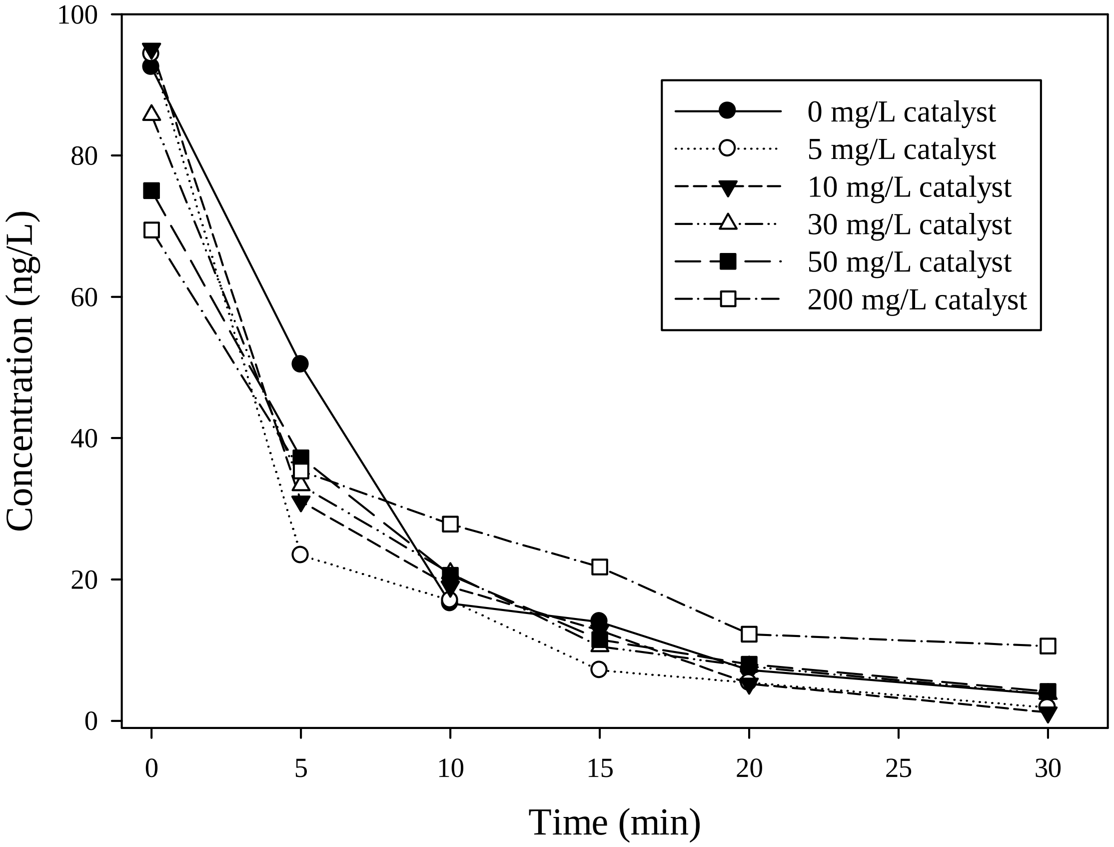


Figure 5.5: Heptachlor photocatalytic degradation in aqueous solutions in the presence of different concentrations of anatase TiO_2, 100 ng/L heptachlor.

With the *k* value calculated, the reaction model can be determined using parameter estimated simulated results. Fig.5.6.B shows the linear correlation between $-\ln(C_t/C_i)$ and time. The oxidation of heptachlor is also represented adequately by the first order kinetics (Eq.5.21)

Table 5.3: Simulated degradation constants for heptachlor oxidation

Catalyst concentration (C_c) (mg/L)	Degradation constant (k)
0	0.1323
5	0.1744
10	0.1508
30	0.1293
50	0.1145
200	0.0794

Mean = 0.1301 Std dev = 0.03228

The effect of *k* for heptachlor degradation can be linearised using an inverse of the catalyst concentration ($1/C_c$). Similarly to DDT oxidation, the *k*-value is decreased with increasing catalyst concentration, it does so with a mathematical equation represented in Eq.5.23, and the rate of reaction expression in Eq.5.24.

$$k = 0.309(1/C_c) + 0.115 \ (r^2 = 0.956) \tag{5.23}$$

$$r = dC/dt = -0.309(1/C_c) + 0.115 \times C \tag{5.24}$$

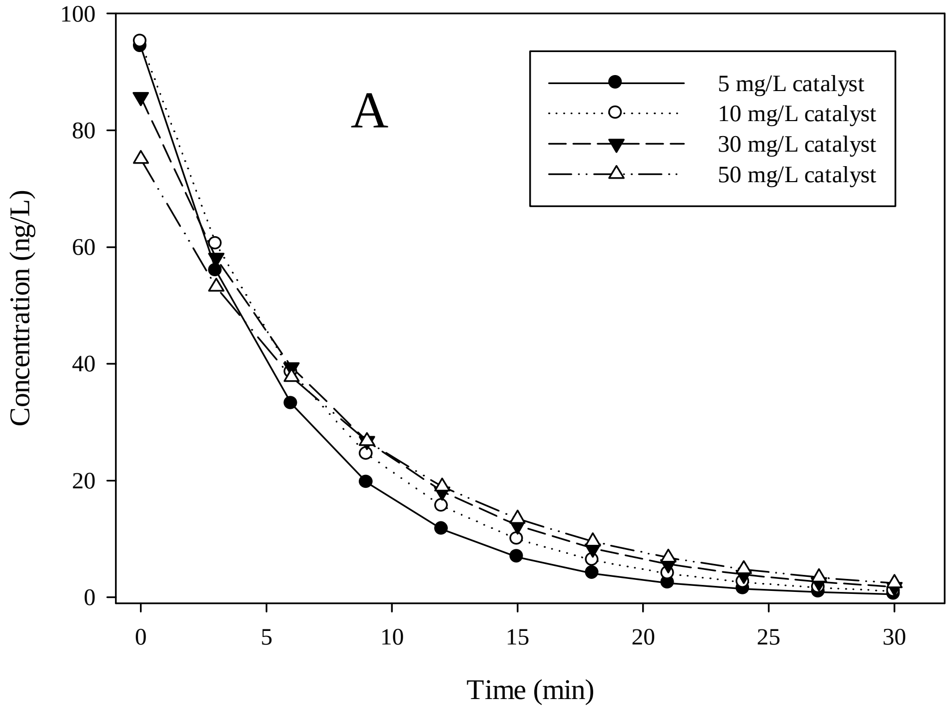


Figure 5.6A: Simulated Heptachlor photocatalysis versus time using TiO_2 catalysis at different concentrations.

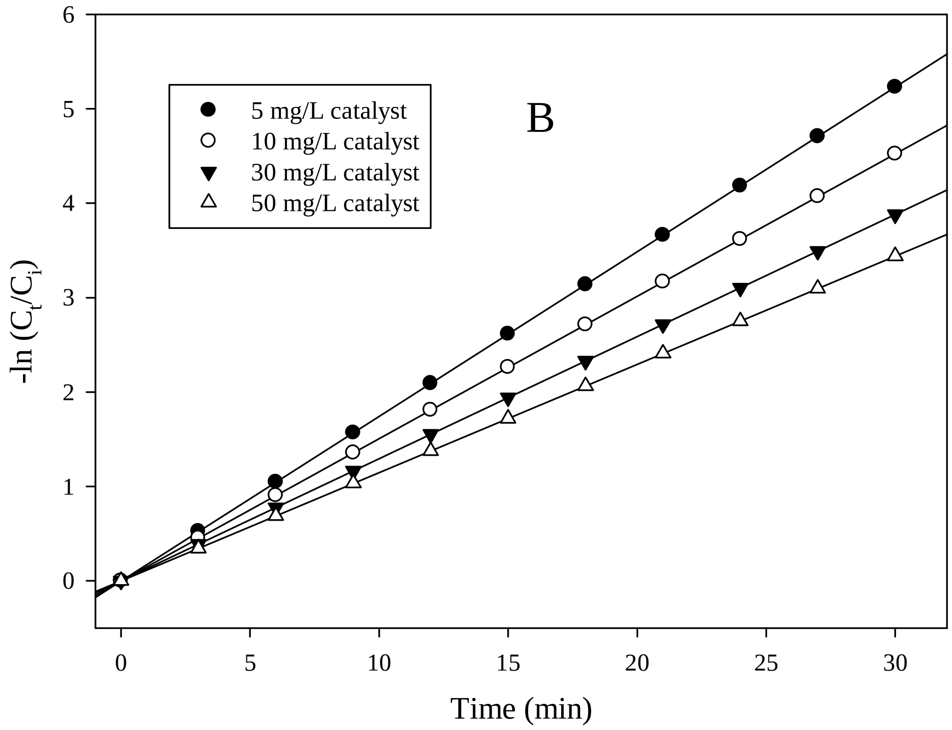


Figure 5.6B: First order rate profiles of Heptachlor photocatalysis using TiO_2 catalyst.

5.3.2.4 Chlordane

The heterogeneous photocatalysed oxidation of chlordane in the presence of the titanium dioxide semiconductor and in the absence of the semiconductor is presented in Fig.5.7. The 5 mg/L catalyst concentration experiment for chlordane produced unusable results and therefore has been omitted from the analytical study. Fig.5.7 is the representation of the degradation of chlordane catalyst at different catalyst concentrations. Fig.5.7 shows that the photocatalyst experiment produced the best mineralisation of chlordane results at the 30 mg/L catalyst concentration, better than the photolytic experiment. The 30 mg/L catalyst experiment shows significantly more efficiency at degrading chlordane in comparison to the other catalyst concentrations. This is a contrast to the results from DDT and heptachlor where catalyst concentrations lower than 30 mg/L showed better chemical removal efficiency. Almost 90 % of chlordane is mineralised within the first 10 minutes of illumination, and near complete degradation is achieved in less than 20 minutes. From Fig.5.7, it can be assumed that catalyst concentration greater than 200 mg/L reach a near state of saturation for chlordane.

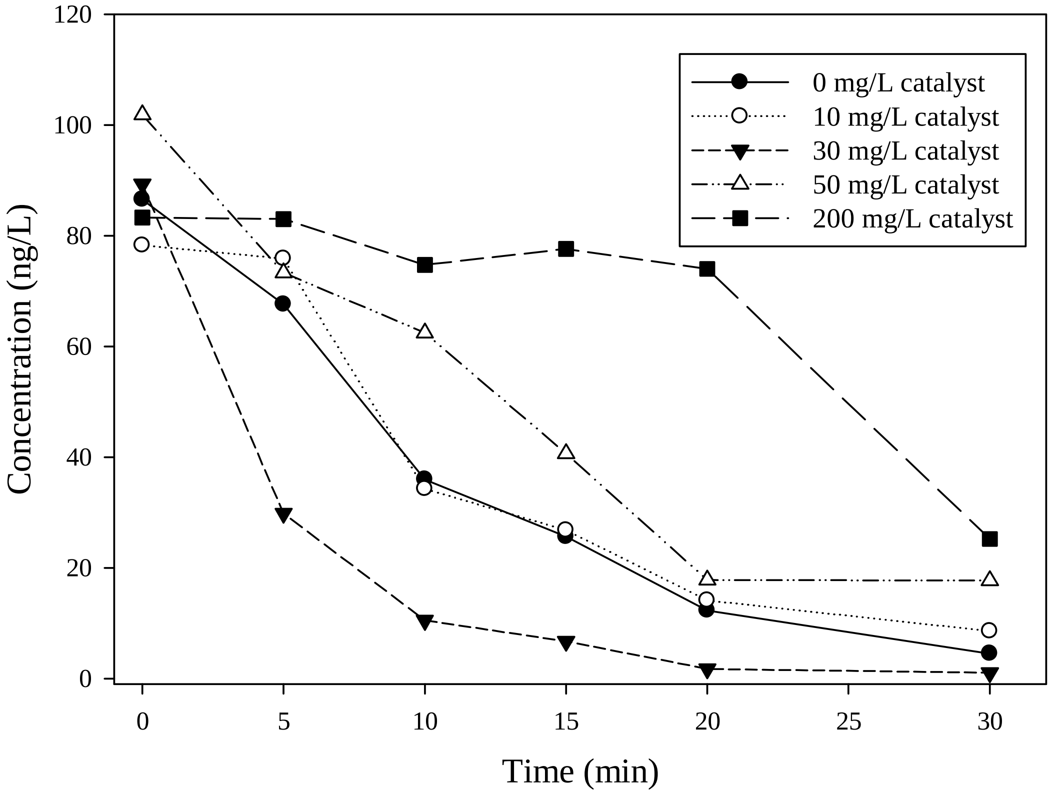


Figure 5.7: Chlordane photocatalytic degradation in aqueous solutions in the presence of different concentrations of anatase TiO_2, 100 ng/L chlordane.

5.3.2.4.1 Evaluating the model of chlordane degradation

Differently to the kinetic determinations of DDT and heptachlor, there was no obvious identified correlation between the catalyst concentration and the reaction rate constants for the heterogeneous photo oxidation of chlordane in the experiments. Table 5.3 gives the rate constants obtained from the experiments. Fig.5.8 shows that the 30 mg/L titanium dioxide catalyst experiment derived the most efficient degradation of chlordane.

Table 5.4: Simulated degradation constants for chlordane oxidation

Catalyst concentration (C_c) (mg/L)	Degradation constant (k)
0	0.0947
10	0.0773
30	0.1957
50	0.0714
200	0.0317

Mean = 0.0942 Std dev = 0.0613

Kinetic simulation produced degradation rate of the photolysis that are better than the 10, 50, and 200 mg/L experiment, this suggest a very narrow range around the 30 mg/L catalyst concentrations for optimal chlordane degradation using titanium oxide under these experiment conditions. These results imply that chlordane oxidation take place in a limited range of catalyst concentrations, approximately at the 30 mg/L catalyst concentrations under the experimental conditions. This is indicated by the similarity in the range of the rate constants below the 10 mg/L catalyst and above the 50 mg/L catalyst concentrations. Ideal chlordane oxidation using titanium oxide can be speculated to occur at optimum catalyst-compound interaction, an optimum catalyst concentration model would need to be developed, to determine the ideal kinetic range.

One of the factors not considered in the reactor activities, are the compound to compound interactions, and compound to catalyst surface site interaction and competition, the latter would be highly dependent on compound reactivity. This alignment of thinking suggest DDE to be the most reactive chemical of the compounds under investigation, as complete degradation in all the experiments took place in less than 5 minutes. The 200 mg/L results depicted stagnant photo oxidation, alluding to the opacity and light scattering being the main contributors to the results, this was also experienced in other analyte compounds at the 200 mg/L catalyst loading. The 200 mg/L results are thus not expected to provide insight on modelling the kinetic parameters of the rate of the reaction.

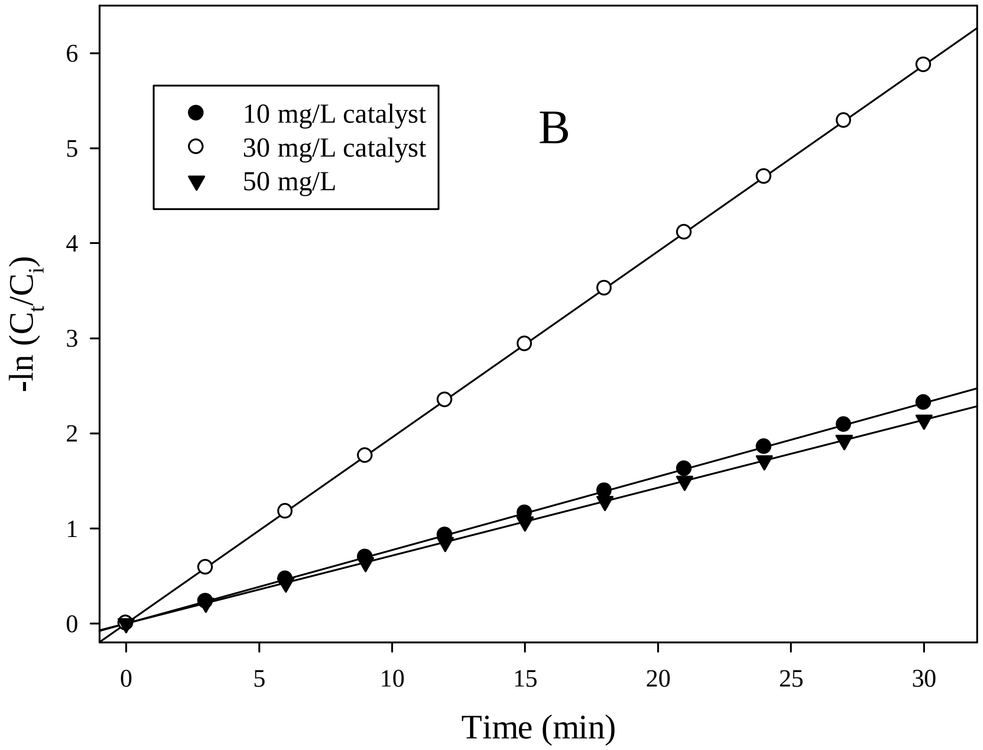


Figure 5.8: First order rate profiles of Chlordane photocatalysis using TiO_2 catalyst.

The kinetic relationship between time and –ln (C_t/C_i) for the photo oxidation of chlordane depicted a linear relationship, meaning that first order reaction kinetics is applicable (Fig.5.8B). As alluded to above, chlordane degradation at these experimental conditions, has a unique catalyst concentration range where mineralisation is achieved with optimum efficiency. It is shown that the 30 mg/L catalyst experiment produced by far the most efficient degradation constant, for this reason the modelled kinetic expression will only take into account the 30 mg/L experiment *k* value. The rate of reaction expression is represented by Eq.5.25.

$$r = dC/dt = - k \times C = - 0.01957k \times C \qquad (5.25)$$

5.3.2.5 Trichlorobiphenyl-2,3,4 (PCB 25)

The heterogeneous photocatalysed oxidation of 2.3.4-Trichlorobiphenyl in the presence of the titanium dioxide semiconductor and in the absence of the semiconductor is presented in Fig.5.9. The semiconductor facilitated photo oxidation of 5 mg/L catalyst concentration is shown to have slightly improved degradation efficiency than the photolytic experiment. Fig.5.9 represents the kinetics of titanium catalysed photo degradation of trichlorobiphenyl. Similarly to DDT and heptachlor, the catalytic efficiency of degradation deteriorates with increasing catalyst concentration. The 5 mg/L catalyst experiment depicted the most favourable degradation of trichlorobiphenyl, 75 % of the compound is mineralised in a 5 minute period. A near zero state of degradation is reached after 10 minutes of irradiation.

In correlation to what was observed in the degradation of DDT and heptachlor, the lower concentrations of 5 and 10 mg/L have better chemical removal rate under the experiment conditions. The 200 mg/L experiment is the least favourable but retains the potential to completely mineralise the chemical in a reasonable time period.

5.3.2.5.1 Evaluating the model of trichlorobiphenyl-2,3,4 degradation

The rate of 2.3.4-Trichlorobiphenyl degradation and the relationship with the catalyst concentration is also represented by Eq.5.19. The degradation constants in different catalyst concentrations are shown in Table 5.4. Simple statistics suggests that there is a slight difference between the photocatalysis experiment of 5 mg/L and photolysis experiment, and even less difference in comparison to the 10 mg/L experiment. The catalytic concentration relationship with degradation rate is calculated using degradation constant values from the 5, 10, 30 and 50 mg/L. The *k*-value is decreased with increasing catalyst concentration, it does so with a linearised mathematical equation represented in Eq.5.26, and the rate of reaction expression in Eq.5.27.

$$k = 0.569(1/C_c) + 0.110 \; (r^2 = 0.973) \qquad (5.26)$$

$$r = dC/dt = -\,0.569(1/C_c) + 0.110 \times C \qquad (5.27)$$

Graphical representation of the kinetic oxidation of trichlorobiphenyl is given in Fig.5.10. First order reaction kinetic principles are elucidated in Fig.5.10B.

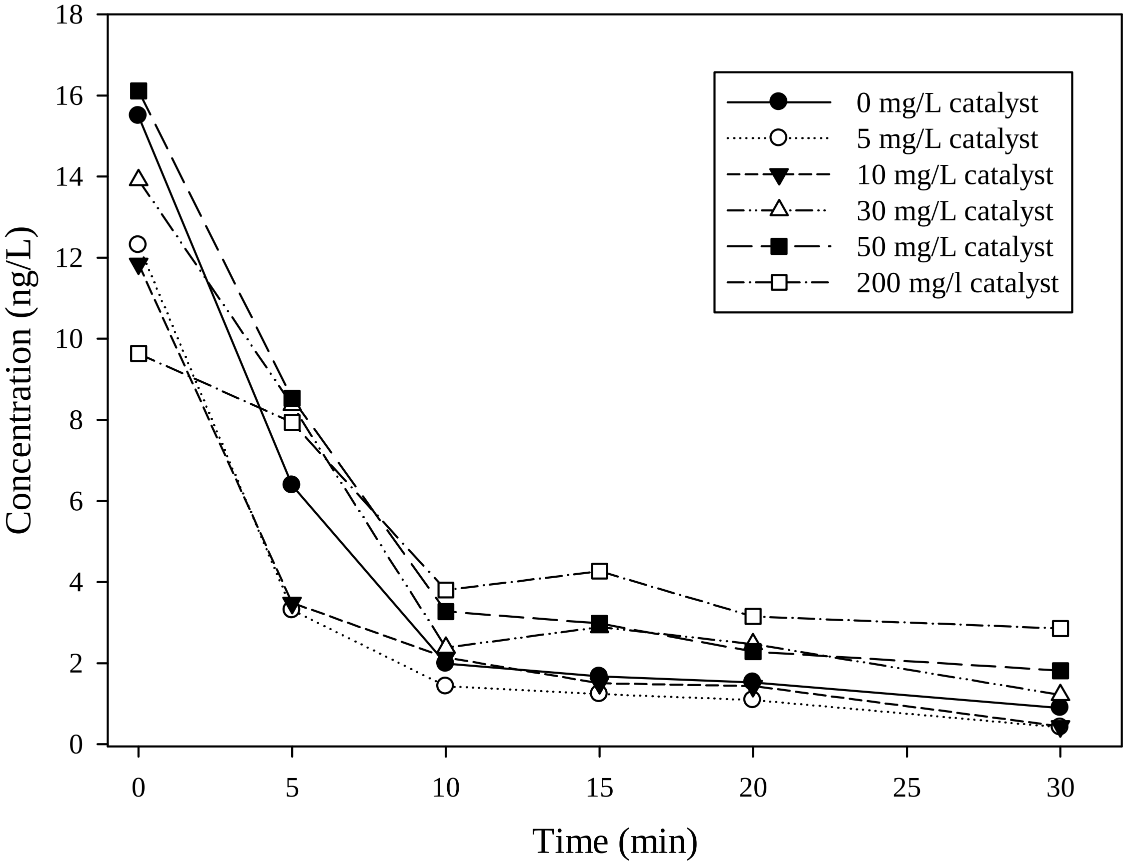


Figure 5.9: Trichlorobiphenyl photocatalytic degradation in aqueous solutions in the presence of different concentrations of anatase TiO_2, 20 ng/L 2,3,4-Trichlorobiphenyl

Table 5.5: Simulated degradation constants for trichlorobiphenyl-2,3,4 oxidation

Catalyst concentration (C_c) (mg/L)	**Degradation constant (k)**
0	0.1719
5	0.2200
10	0.1784
30	0.1233
50	0.1215
200	0.0563

Mean = 0.1630 Std dev = 0.0414

5.4 Comparative kinetics

Table 5.6 shows the tabulated values of the degradation studies. A modelled degradation constant was calculated using all data acquired from each compound study.

Table 5.6: First order rate analysis for OCs photocatalytic degradation using TiO_2

Compound	**Photocatalytic performance**			**Photolysis performance**
	***k*-value**	**Max, k-value**	**Std error**	
DDT	0.142	0.2646	0.010	0.1551
Heptachlor	0.141	0.1744	0.004	0.1323
Chlordane	0.095	0.1957	0.010	0.0947
PCB 25	0.149	0.2200	0.011	0.1719

5.4.1 Model accuracy

Fig.5.11 shows the graphical representation of the simulated photocatalyst performance experiments in comparison to the modelled plot. In each case, the best and the worst performing photocatalyst experiments are shown. As alluded to earlier, the best performing catalyst concentration in most compound experiments was the 5 mg/L, with the exception of chlordane, where the 30 mg/L experiment performed the best. The observed trend of the DDT, heptachlor and trichlorobiphenyl experiments was decreased reactivity with increased catalyst concentration. The 200 mg/L experiments in the study depicted less conformed results, hence the 50 mg/L catalyst concentration experiments were used comparatively. The 50 mg/L concentrations depicted the least efficient degradation while upholding the principles of the oxidation process. DDT, chlordane and trichlorobiphenyl experiments suggest significant difference in the degradation constants between photolysis and the best performing catalyst concentration of the photocatalysis experiments.

Table 5.6 shows the *k*-values of photolysis and the maximum photocatalytic *k*-value. The heptachlor degradation experiment shows better favoured degradation efficiency under photocatalytic conditions, but the degradation constants do not differ significantly. Even the modelled kinetic curve does not show significant difference from the best and worst performing oxidation experiments.

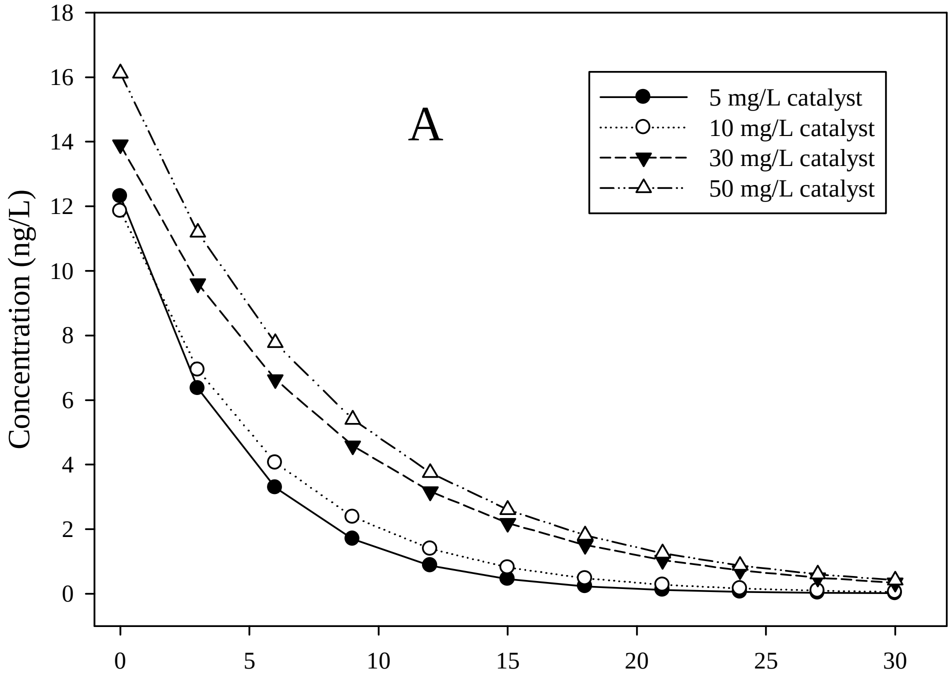


Figure 5.10A: Simulated 2.3.4-trichlorobiphenyl photocatalysis versus time using TiO_2 catalysis at different concentrations.

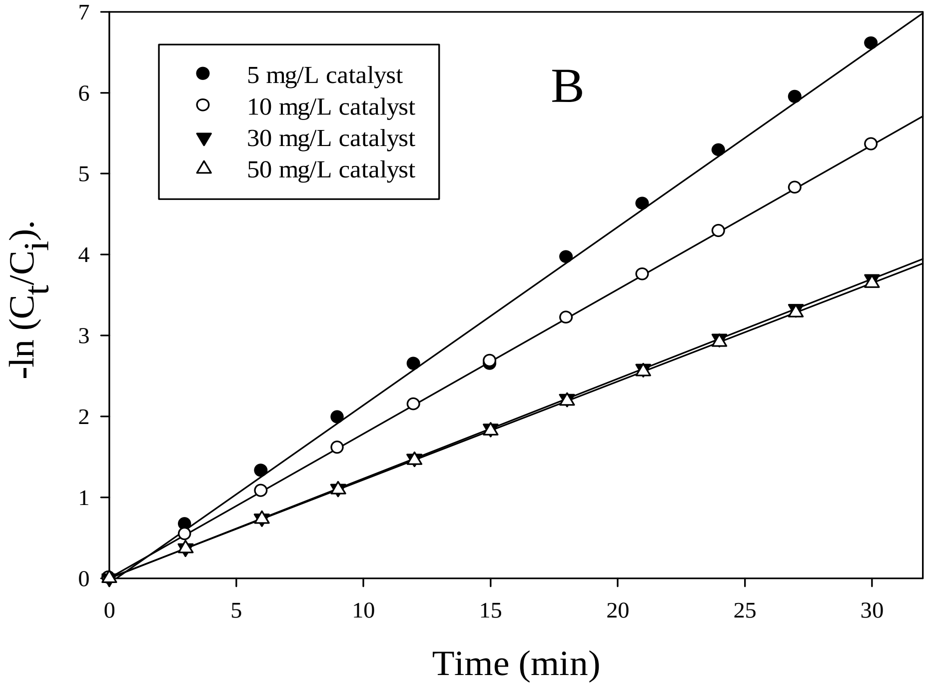
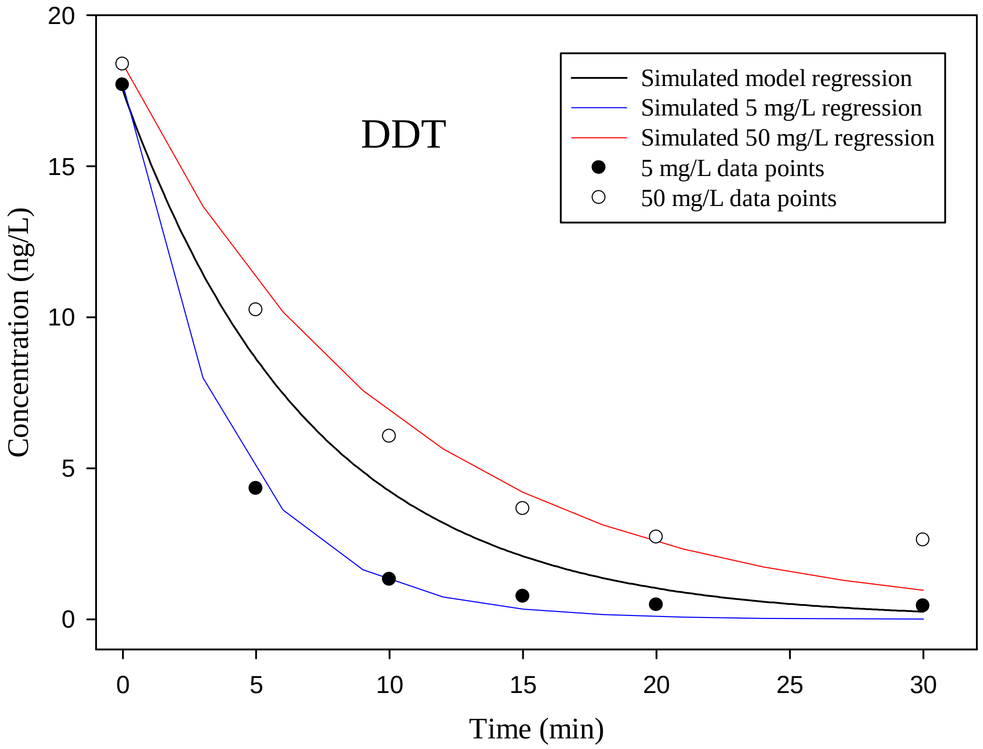
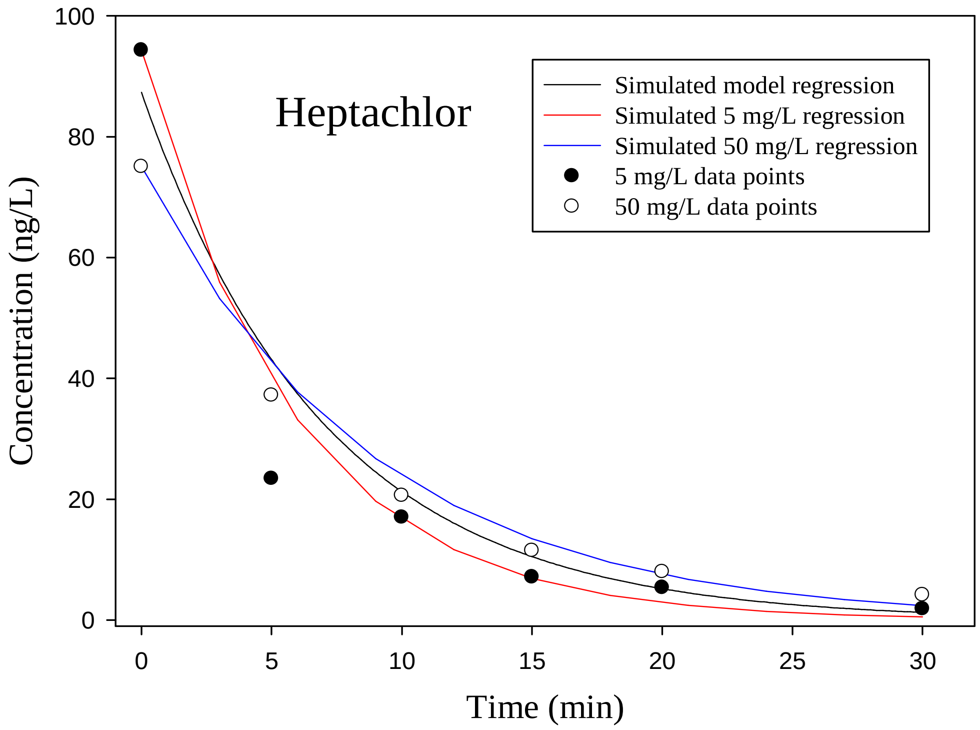
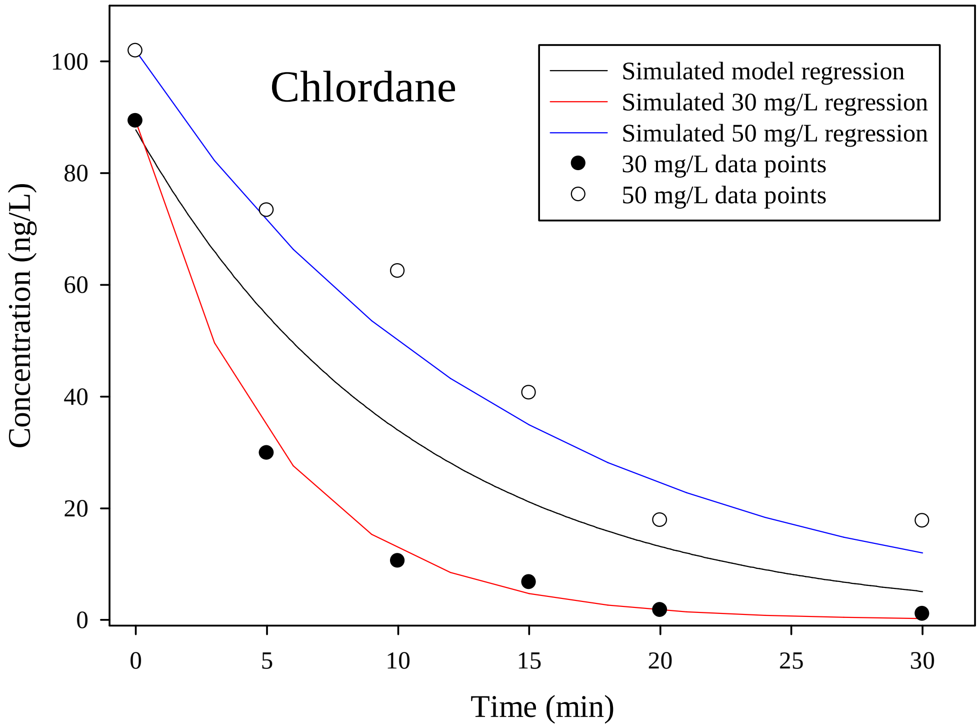


Figure 5.10B: First order rate profiles of 2.3.4-trichlorobiphenyl photocatalysis using TiO_2 catalyst.


DDT
Concentration (ng/L)
Time (min)
0
5
10
15
20
0
5
10
15
20
25
30
Simulated model regression
Simulated 5 mg/L regression
Simulated 50 mg/L regression
● 5 mg/L data points
○ 50 mg/L data points


Heptachlor
Concentration (ng/L)
Time (min)
0
20
40
60
80
100
0
5
10
15
20
25
30
Simulated model regression
Simulated 5 mg/L regression
Simulated 50 mg/L regression
● 5 mg/L data points
○ 50 mg/L data points



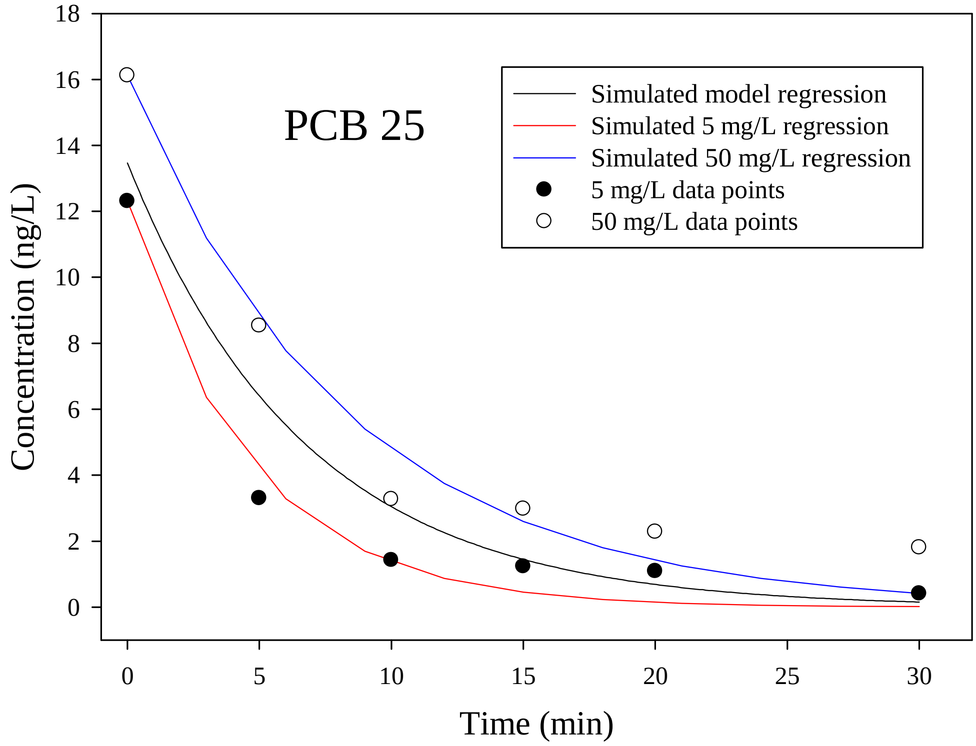


Figure 5.11: Simulated comparative degradation kinetic curves of DDT, heptachlor, chlordane and 2.3.4-trichlorobiphenyl, at different TiO_2 catalyst concentrations.

5.5 Performance of copper oxide doped TiO_2 catalyst

The degradation efficiency of copper oxide surface modified titanium oxide catalysts was investigated in the photocatalytic oxidation of organochlorinated chemicals dissolved in aqueous solutions. The compounds investigated in this section of the section were 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (DDT) and heptachlor, selected as the best representatives in the study as these showed the best conformed data of exponential degradation in the undoped experiments under the experimental conditions. The preparation of the catalyst solutions investigated included different processing techniques, where the same concentration of copper dopant were sonicated in one set of experiments and not sonicated in the other set.

The raw catalyst findings used for comparative analysis were imported from the photocatalytic results. The semiconductor catalyst concentrations used were 10 and 30 mg/L, these were chosen based on the nature of the findings evident in the photocatalysis study, where the catalyst degradation affinity differed significantly from the lower concentrations (below 10 mg/L) to the higher concentration (above 30 mg/L).

The surface modification procedure used in this study was not as extensive at the some reported in literature by Li et al., (2008), Chiang et al., (2002), Choi et al., (1994), and others. Most of the methods in literature tend to follow the nano-technological route of preparation, and the aim of this study was not to focus significantly on the surface modification of the catalyst but instead apply the principles used in photocatalysis to investigate the hypothesis.

5.5.1 Organochloride compounds

The results of the 30 mg/L catalyst concentrations investigation represented in Fig.5.12 and Fig.5.13 suggest that heterogeneous systems of doped catalyst to be more photoactive than the undoped. Fig.5.12 shows a comprehensive efficiency of DDT removal (k = 0.2002) in the unsonicated doped catalyst in comparison to the raw anatase titanium oxide (k = 0.1189). After irradiation of 5 minutes, about 65 % of DDT had been degraded, where-as at the same period, only about 44 % of DDT had been removed by the undoped catalyst. The doped catalyst reached a near zero steady state post the 10 minute sampling interval where almost 95 % of DDT had been removed. After the illumination period of 30 minutes, only about 80 % of DDT had been mineralised by non surface modified catalyst. It is evident from Fig.5.12

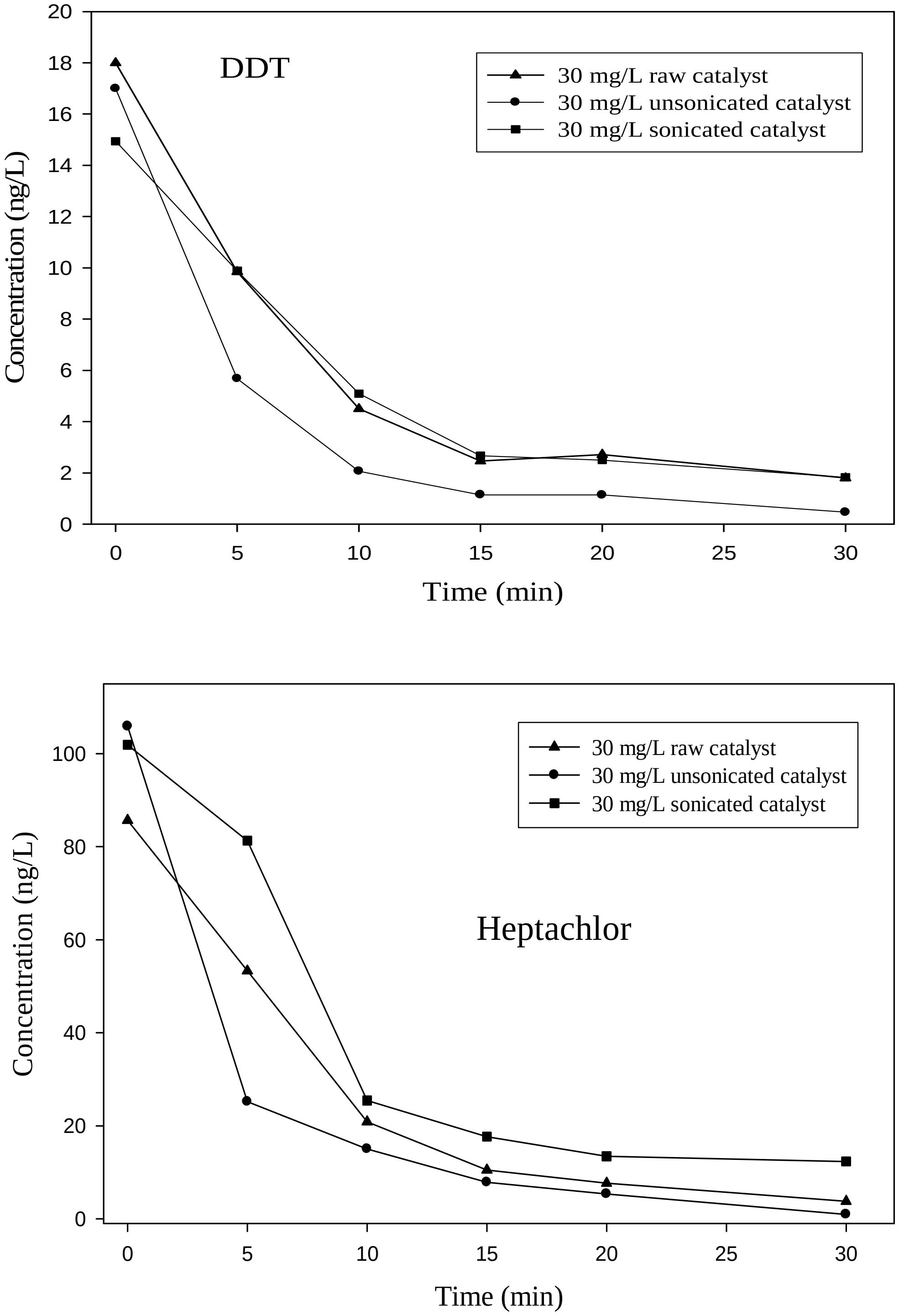


Figure 5.12: Kinetics of DDT and heptachlor photocatalytic degradation in aqueous solutions in the presence of undoped and 30 mg/L copper oxide doped anatase TiO_2, 20 ng/L DDT and 100 ng/L heptachlor compounds.

that the copper oxide dopant is affected by sonication before photocatalysis, and the results also suggest no improvement in the catalyst ability to oxidise DDT at the catalyst concentrations of 30 mg/L, the sonicated doped catalyst recorded values closely related to the undoped catalyst. Fig.5.12 also shows the photocatalytic removal of heptachlor from aqueous solutions at catalyst concentrations of 30 mg/L. In correlation to DDT removal, the unsonicated doped catalyst depicts the most efficient degradation of heptachlor. A 5 minute irradiation period eliminated over 75 % of heptachlor, while the undoped catalyst and the sonicated doped catalyst only removed 38 % and 20% respectively. Near complete mineralisation of heptachlor by the unsonicated doped catalyst was reached in less than 20 minutes, followed closely by the raw catalysts. Analogous to DDT, the sonicated doped catalyst shows the least favourable results. These results indicate a decrease in oxidation ability of doped sonicated copper catalyst in degrading heptachlor, to extents even less favourable than raw anatase TiO_2 in aqueous solutions.

The results of the 10 mg/L catalyst concentrations investigation are represented in Fig.5.13. Fig.5.13 suggests a slightly modified picture of the heterogeneous systems of doped catalyst. It maintains minor advantage to the doped catalyst being more photoactive than the undoped. After 5 minutes of radiation, the doped unsonicated and sonicated catalysts, and the undoped all depict around 50 % DDT removal. At the 10 minute point the removal efficiencies of DDT were still closely matched, the undoped catalyst recording 81 %, the doped sonicated catalyst recording 87 %, and the doped unsonicated catalyst recording 90%. The results suggest the unsonicated doped catalyst to still be the more favourable in comparison, at the 15 minute mark slightly over 97 % of the DDT is removed, where-as the doped sonicated and the undoped catalyst reach this point beyond the 30 minutes radiation period.

The raw titanium oxide catalyst is shown to be the more favourable at degrading heptachlor in the earlier periods of UV illumination. At the 10 minute sampling interval the undoped catalyst removed 89% of heptachlor, in the same period 74 % and 81 % had been respectively degraded by the doped sonicated and unsonicated catalyst. At the 15 minutes stage Fig.5.13 also shows that the raw and the doped unsonicated catalysts more favourable, eliminating 92% and 93 % of heptachlor respectively, near complete degradation is achieved within 30 minutes of irradiation.

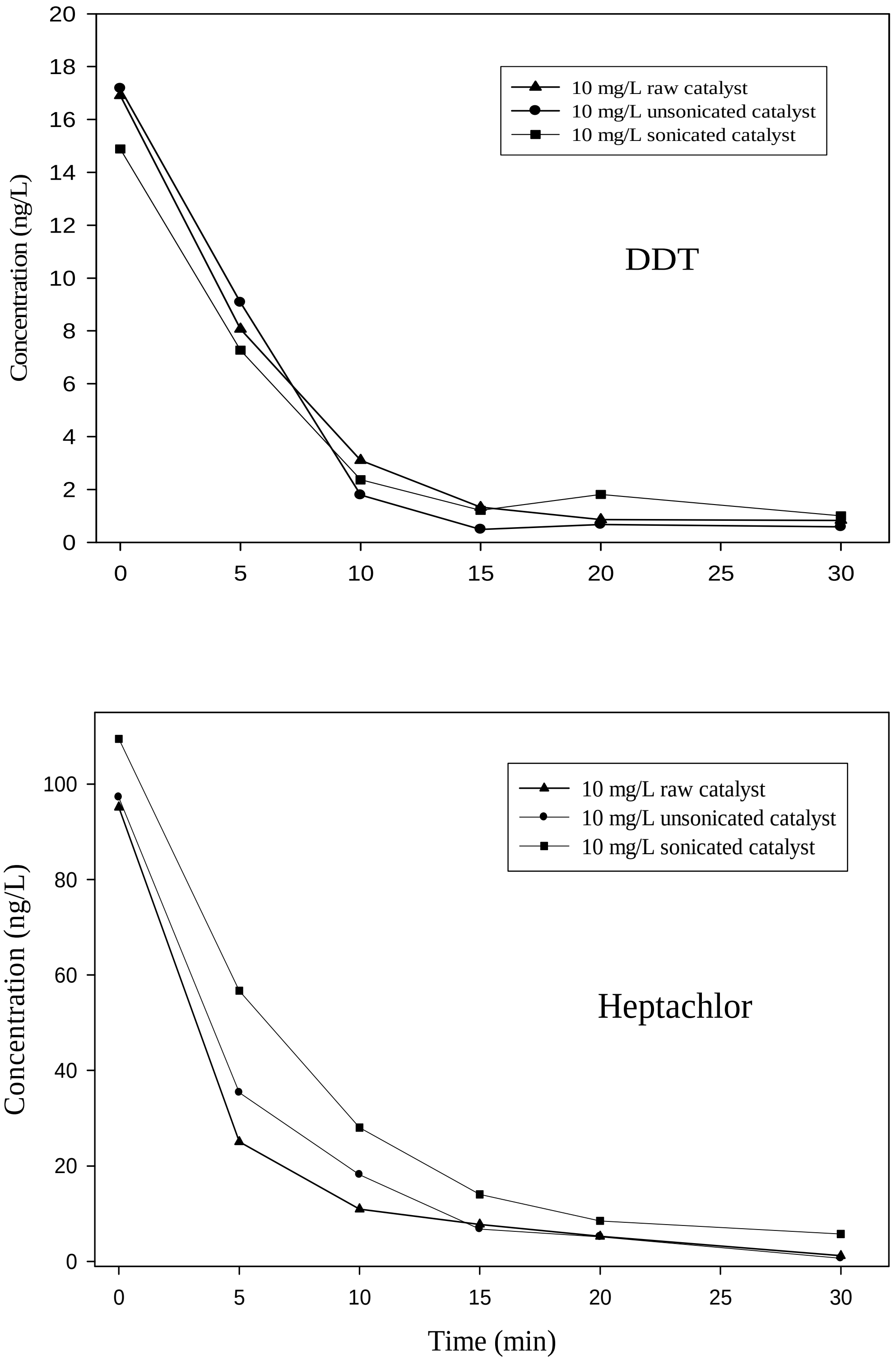


Figure 5.13: Kinetics of DDT and heptachlor photocatalytic degradation in aqueous solutions in the presence of undoped and 10 mg/L copper oxide doped anatase TiO_2, 20 ng/L DDT and 100 ng/L heptachlor compounds.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

One of the objectives of this study was to determine the prominence of organochloride compound in the environment. Samples were collected from wastewater treatments plants and local dams. The results revealed elevated concentrations of organochlorinated chemical pollution in most of the analysed water samples. The results acquired from the study are a reflection of the sum of agricultural soils embedded chemicals and the circulating chemicals in the aquatic environment. The wastewater samples generally recorded higher concentration in comparison to the dam samples, indicating a greater concentration of dissolved chemicals in rain water runoff than in settled surface waters. The difference can be speculated to be attributed by soil embedded chemicals.

The concentrations yielded by this study were significantly higher than those stipulated by the South African water quality guidelines, which are less stringent than accepted international standards. These results show the seriousness of the issue of endocrine disruptive chemicals in surface waters, and reemphasises the need to develop treatment technologies. More-over, the concentration levels recorded in this study echoes the need to promptly invest research in this discipline. Increasing numbers of chemicals are produced from all parts of the world, and many are found to constitute endocrine disruptive properties. This in essence means that if the scientific community is to deal with this issue, rapid proactive measures need to be undertaken to characterise the existing compounds and the methods amenable to their treatment, otherwise technology will continuously be reactive and this is dangerous when dealing with human lives.

The main subject of this study was to investigate the application of heterogeneous photocatalytic oxidative processes in complete degradation of organochlorides, using TiO_2 as a semiconductor metal ion. This was hypothesised to be more efficient at degrading organochloride compounds than conventional photolysis. Photocatalytic degradation using TiO_2 catalyst has been demonstrated to completely mineralising organic compounds dissolved or dispersed in water and wastewater. The study findings showed that photocatalysis using titanium dioxide as a catalyst has an improved efficiency of removal in comparison to photolytic degradation. DDT, heptachlor, and trichlorobiphenyl depicted similar results in the mineralisation process. The catalyst concentration of 5 mg/L produced the most favourable results in these experiments, achieving near 100 % removal of these compounds in less than 15 minutes of irradiation. It was also observed that increased catalyst concentration reduced the degradation efficiency of these compounds. The photocatalysis of chlordane produced results contrasting the catalyst findings in the DDT, heptachlor and trichlorobiphenyl experiments. Chlordane analysis showed the 30 mg/L catalyst concentration experiment to be the most favourable, and degradation at lower or higher concentrations was significantly hampered. This alludes to a compound-catalyst specific relationship, further investigation would provide better insight. The 30 mg/L catalyst concentration achieved complete degradation of chlordane in less than 30 minutes. It was generally found that within an appropriate range, photocatalyst concentration led to higher reaction efficiency for most compounds under the experimental conditions. It can also be speculated that excessive catalyst application results in much reduced efficiencies. This was evident from the 200 mg/L catalyst experiments, which showed significantly reduced degradation of most organochlorides under study. This is thought to be caused by illumination hindrance resulting from light scattering and thus decrease in the passage of irradiation through the solution.

The photo oxidation of DDE did not provide much insight on the degradation dynamics. Near complete mineralisation at all catalyst concentration was achieved approximately 5 minutes into the illumination process. There were no observable differences in catalytic degradation of the chemical at difference catalyst concentrations post the 5 minute sampling interval with the exception of the 200 mg/L concentration. It can be assumed that there is photocatalytic variability within the 5 minute period for DDE degradation.

Even though heterogeneous photocatalysis using TiO_2 as a semiconductor has been demonstrated to be efficient at degrading most organic compounds, some draw-backs have been documented in the photocatalysis method. The main draw-back being the inability of titanium dioxide to facilitate oxidation at ambient temperatures, as the band-gap energy required is still significantly greater. One of the more frequently recommended solutions to reduce the energy band-gap is to modify the titania surface structure, resulting in a narrow TiO_2 energy band-gap. Having achieved improved degradation of organochloride compounds using photocatalysis principles, this study attempted to further improve the mineralisation efficiency of the process through titanium dioxide surface modification.

Surface modification of titanium dioxide using metal oxides has been documented to reduce the band-gab by interfering with the carrier charge transfer process, allowing for oxidation-reduction reactions to take place at improved efficiencies. Copper oxide was used as a metal ion in the process of surface modifying the TiO_2 molecules. A simple non elaborate procedure was conducted modified from literature studies. Comparative results were acquired from an undoped catalyst and a copper doped catalyst, a third variable emanated from the doping method followed in the study, of reducing the particle size of the doped solution to achieve smaller particle radii as the processed matter appeared aggregated. A sonication step was included in the experimental method, and this served as another variable.

Unsonicated copper oxide doped TiO_2 catalyst was found to be the most efficient degrading form. This was evident at both catalyst concentration of 30 mg/L and 10 mg/L for DDT in comparison to raw anatase and the sonicated doped form. It presented efficiency significantly greater in the 30 mg/L concentration than in the 10 mg/L concentration. In most experiments, complete mineralisation was achieved in fewer than 15 minutes. The heptachlor degradation analysis showed the doped unsonicated experiment at 30 mg/L catalyst concentration more favourable, however, the results in the 10 mg/L experiments were not definitive. These findings are in agreement with documented literature stating an improved removal of organic chemicals dissolve and suspended in aqueous systems using doped catalyst. It can thus be concluded that the process of surface modifying the structure of the titania oxide particles using copper oxide does reduce the band-gap energy allowing for improved photocatalytic efficiencies in degrading polyorganochlorinated compounds is aqueous systems.

The results obtained from the photocatalytic studies were encouraging and showed photocatalysis to be a viable mineralisation method. Using a designed reactor with standard parameters of heterogeneous photocatalysis, mathematical models were investigated for the organochlorinated compounds of interest. Experimental data was simulated to estimate the rate of compound degradation. All parameters were kept constant, with the exception of the TiO_2 catalyst concentration, with the assumption that only the catalyst concentration would have an effect on the rate of degradation. The degradation rate constant generally decreased with increased catalyst concentration above the 5 mg/L catalyst, with the exception of chlordane which had a range in the 30 mg/L region, meaning that optimum removal was best achieved in a narrow range of catalyst concentrations. It was found that the degradation process depicted first order reaction kinetic for the compounds under study. A mathematical model was proposed for scale-up and design of these types of photo reactors with respect to the catalyst concentration. The model was compared to the experimental results and was found to fit the experimental results satisfactorily within the ranges of the parameter investigated. The kinetic reaction models provided can be used to calculate the scale-up parameters for the method installations. The model provides a simple solution to designing and developing photocatalytic oxidation technology for water and wastewater treatment.

6.2 Recommendations

In the conducted study, there are areas which can be considered for future research. One of the primary shortfalls that exist in slurry catalyst application is that that of catalyst reclamation and possible reuse. Due to the fine particle nature of the TiO_2 semiconductor catalyst, it is challenging to reclaim by conventional methods. One of the methods which have been proposed which can be further explored is membrane technology. Another more promising technology is surface mounted crystals of the semiconductor, further research into these subjects has the potential to overcome the reclamation drawbacks.

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APPENDIX A

```
************************************************************************

AQUASIM Version 2.0 (win/mfc) - Listing of System Definition

************************************************************************

DDT degradation experiment, TiO2 catalyst concentration of 5 mg/L



************************************************************************
Variables
************************************************************************
C:             Description:          conc
               Type:                 Dyn. Volume State Var.
               Unit:                 nG/L
               Relative Accuracy:    1e-006
               Absolute Accuracy:    1e-006
------------------------------------------------------------------------
C_meas:        Description:          real conc
               Type:                 Real List Variable
               Unit:                 nG/L
               Argument:             t
               Standard Deviations:  global
               Rel. Stand. Deviat.:  0.03
               Abs. Stand. Deviat.:  0.1
               Minimum:              0
               Maximum:              1e+009
               Interpolation Method: linear interpolation
               Sensitivity Analysis: active
               Real Data Pairs (6 pairs):
                  0               12.3079
                  5               3.3071
                  10              1.4274
                  15              1.2339
                  20              1.0884
                  30              0.4136
------------------------------------------------------------------------
k:             Description:          rate constant
               Type:                 Constant Variable
               Unit:                 1/min
               Value:                0.22000344
               Standard Deviation:   0.029367094
               Minimum:              0
               Maximum:              10
               Sensitivity Analysis: active
               Parameter Estimation: active
------------------------------------------------------------------------
t:             Description:          time
               Type:                 Program Variable
               Unit:                 min
               Reference to:         Time
************************************************************************
```

```
************************************************************************
Processes
************************************************************************
Degradation:   Description:          Oxidation
               Type:                 Dynamic Process
               Rate:                 k*C
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C : -1
************************************************************************
Compartments
************************************************************************
Mixed:         Description:
               Type:                 Mixed Reactor Compartment
               Compartment Index:    0
               Active Variables:     C
               Active Processes:     Degradation
               Initial Conditions:
                 Variable(Zone) : Initial Condition
                 C(Bulk Volume) : C_meas
               Inflow:               0
               Loadings:
               Volume:               100
               Accuracies:
                 Rel. Acc. Q:        0.001
                 Abs. Acc. Q:        0.001
                 Rel. Acc. V:        0.001
                 Abs. Acc. V:        0.001
************************************************************************
```

```
************************************************************************
Definitions of Calculations
************************************************************************
calc1:         Description:
               Calculation Number:   0
               Initial Time:         0
               Initial State:        given, made consistent
               Step Size:            3
               Num. Steps:           10
               Status:               active for simulation
                                     active for sensitivity analysis
************************************************************************
```

```
************************************************************************
Definitions of Parameter Estimation Calculations
************************************************************************
fit1:          Description:
               Calculation Number:   0
               Initial Time:         0
               Initial State:        given, made consistent
               Status:               active
               Fit Targets:
                 Data : Variable (Compartment,Zone,Time/Space)
                 C_meas : C (Mixed,Bulk Volume,0)
***********************************************************************
```

```
************************************************************************
Plot Definitions
************************************************************************
plot1:         Description:
               Abscissa:             Time
               Title:
               Abscissa Label:       Time (min)
               Ordinate Label:       Conc (nG/L)
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : C [0,Mixed,Bulk Volume,0]
                 Value : C_meas [0,Mixed,Bulk Volume,0]
************************************************************************
```

```
************************************************************************
Calculation Parameters
************************************************************************
Numerical Parameters:    Maximum Int. Step Size:  1
                         Maximum Integrat. Order: 5
                         Number of Codiagonals:   1000
                         Maximum Number of Steps: 1000
------------------------------------------------------------------------
                         Fit Method:              secant
                         Max. Number of Iterat.:  100
************************************************************************
```

```
************************************************************************
Calculated States
************************************************************************
Calc. Num.  Num. States  Comments
0           6            Range of Times: 0 - 30
************************************************************************
```

APPENDIX B

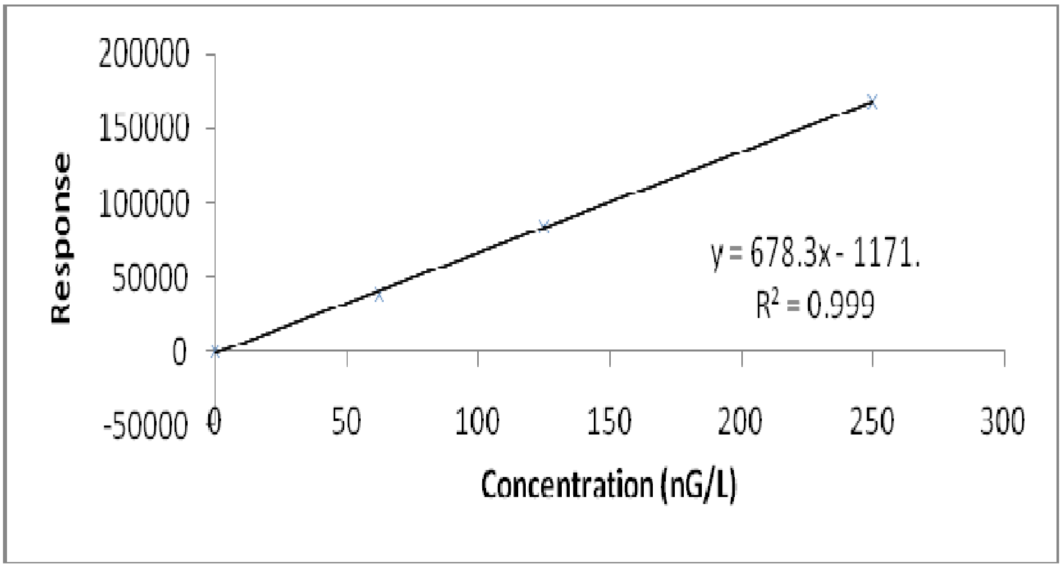

Figure B1: Chlordane calibration graph, methanol solvent

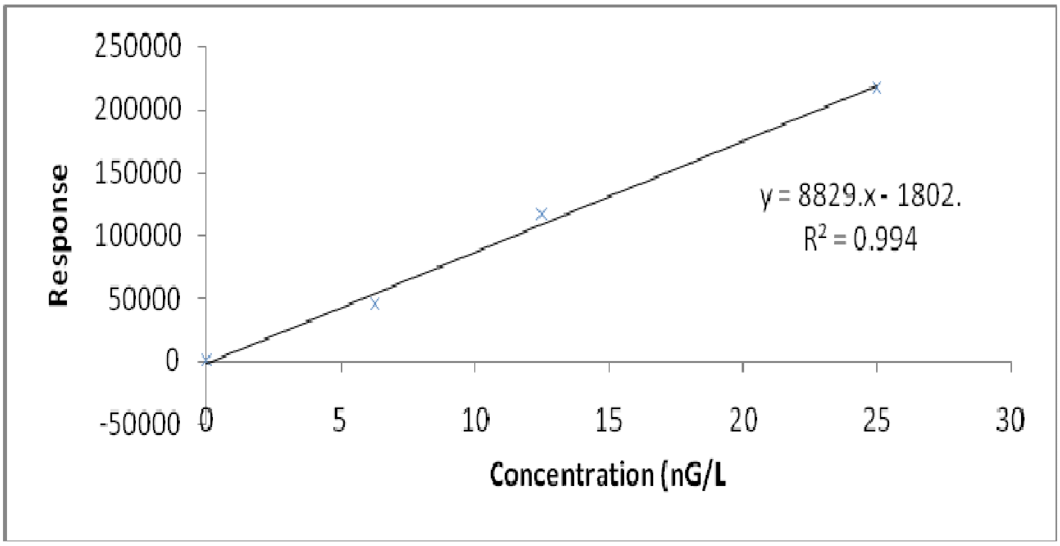

Figure B2: DDT calibration graph, methanol solvent

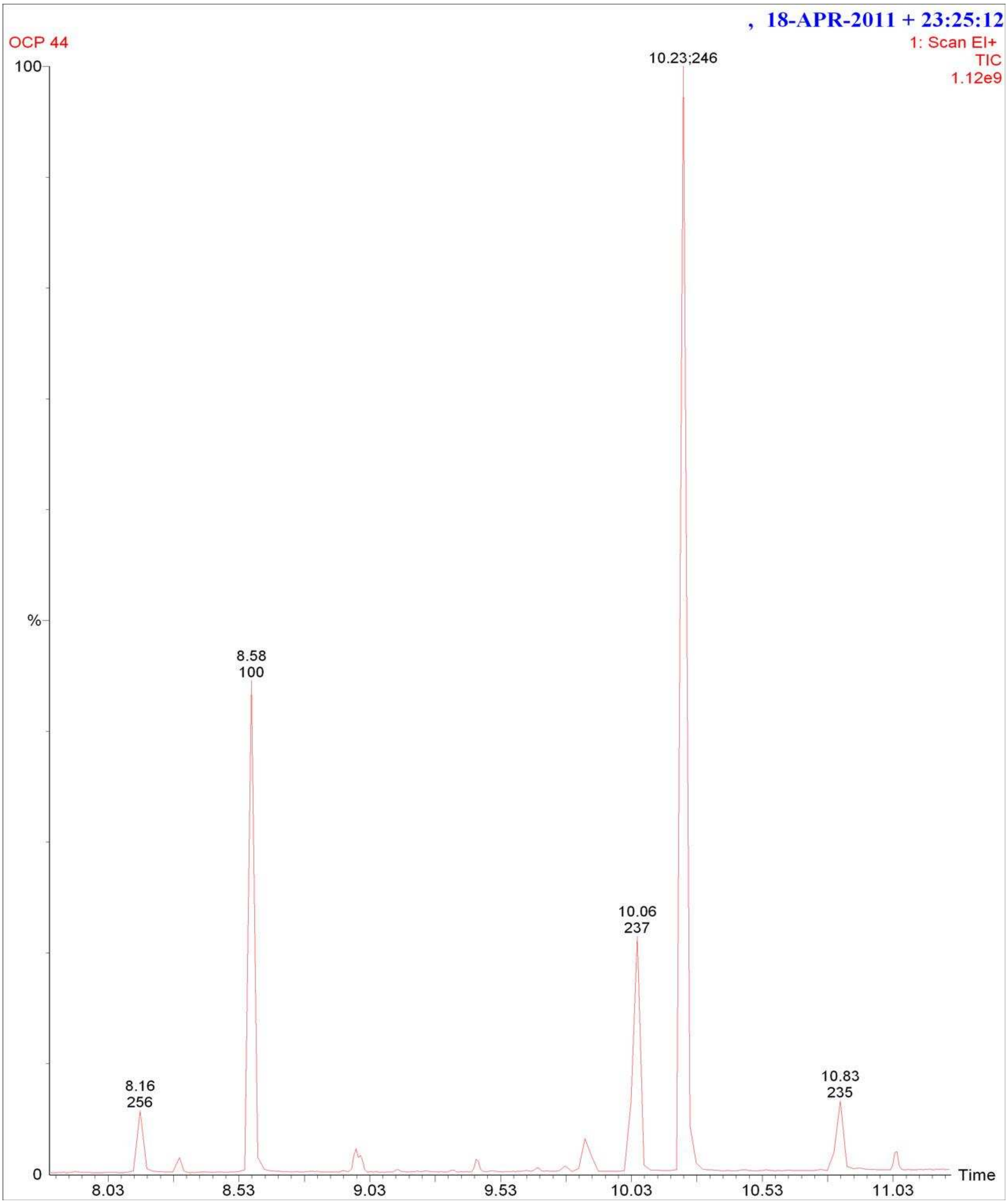

Figure B3: Compound chromatogram, Retention times 8.16, 8.58, 10.06, 10.23, and 10.83 respectively represent 2.3.4.Trichlorobiphenyl, heptachlor, chlordane, DDE, and DDT.

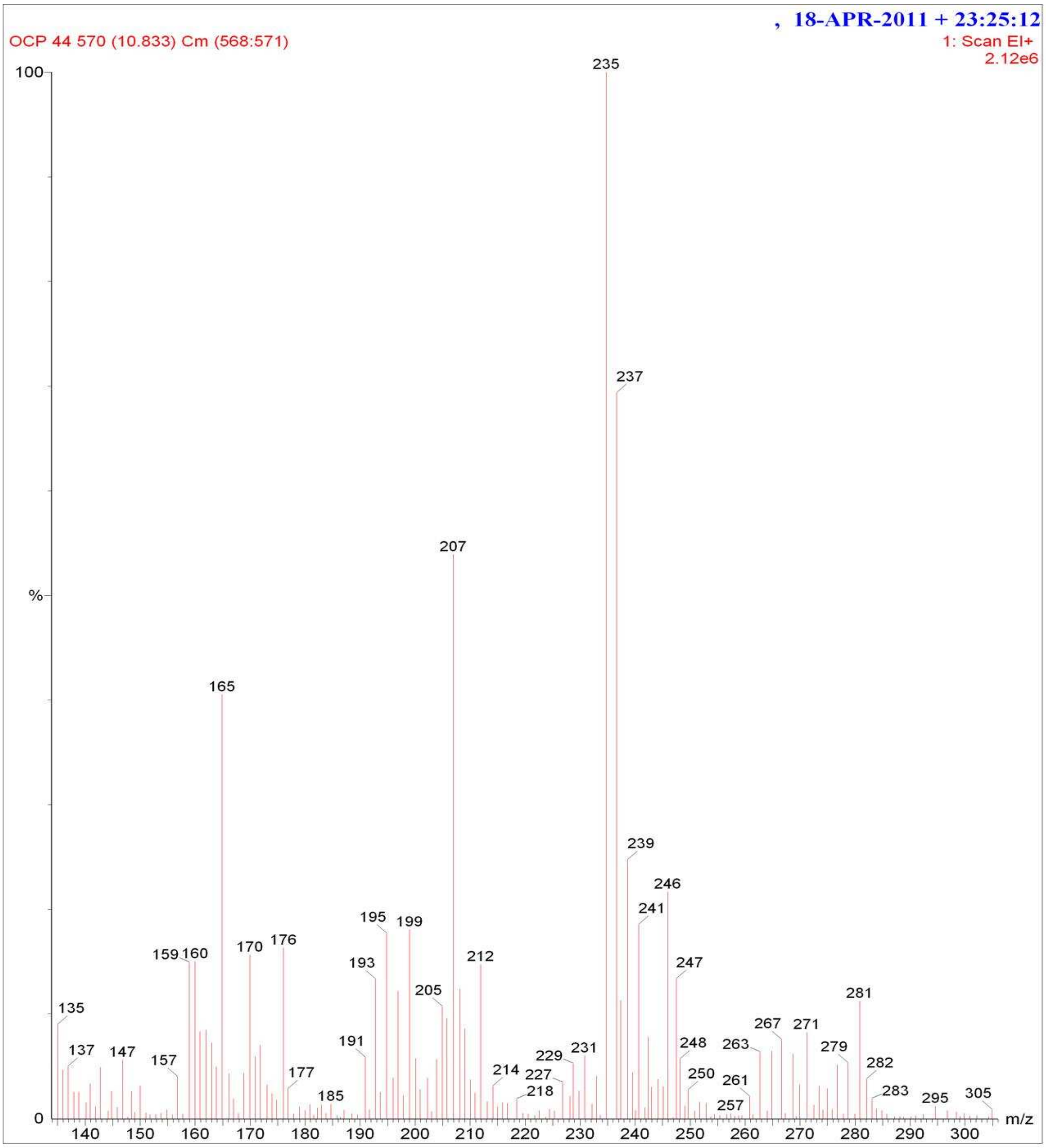

Figure B4: DDT spectrum list