# Development of Titanium Dioxide composites for the removal of pesticides from water using photocatalysis

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A thesis submitted for the degree of Doctor of Philosophy

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# Abstract

The EU Water Framework Directive (WFD) specifies that measures must be adopted against contamination of water by pollutants presenting a significant risk to the aquatic environment. Annex VIII of the directive provides an indicative list of the main pollutant types in water systems, where specific reference is made to "biocides and plant protection products". Pesticides are widely used and have the potential to enter surface waters and cause harmful effects to both humans and the environment. This project focuses on the removal of two such pesticides (4-Chloro-2-methylphenoxy acetic acid (MCPA) and 2,4-Dichlorophenoxy acetic acid (2,4-D) from water using three different titanium dioxide ($TiO_2$) composites. The first composite is based on activated carbon and $TiO_2$ illuminated with UV light. The second composite is based on the combination of dyes (porphryrin/methylene blue) and $TiO_2$ to enhance the photocatalytic properties of $TiO_2$ under visible light. The third composite is composed of dolomite and $TiO_2$. Overall, while the pesticide removal rates using each of the three composites do not show any improvement over existing technologies, there have been a number of interesting findings that indicate scope for further work, particularly in $TiO_2$ photocatalysis analysis.

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## *Poster Presentations*

"Development of novel adsorbents for the removal of selected endocrine disrupting compounds from water and wastewater using photocatalysis" R. O' Dwyer, J. Tobin, K. Nolan A. Morrissey, 20th Irish Environmental Researchers' Colloquium, Limerick (Ireland), 2010

"Development of novel adsorbents for the removal of selected endocrine disrupting compounds from water and wastewater using photocatalysis" R. O' Dwyer, J. Tobin, K. Nolan A. Morrissey, Biannual Meeting, Questor Centre, Queens University, Belfast (Northern Ireland) May 2010

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"Development of novel photosensitisers for the removal of selected Endocrine disrupting compounds from water and wastewater using photocatalysis" R. O' Dwyer, J. Tobin, K. Nolan A. Morrissey, DCU Questor Internal workshop, March 2011

"Development of novel photosensitisers for the removal of selected Endocrine disrupting compounds from water and wastewater using photocatalysis" R. O' Dwyer, J. Tobin, K. Nolan A. Morrissey, 21st Irish Environmental Researchers' Colloquium, University College Cork, April 2011

"Development of $TiO_2$ composites for the removal of pesticides from water and wastewater using photocatalysis" R. O' Dwyer, J. Tobin, K. Nolan A. Morrissey, ISPE Ireland Affiliate Plant Tour & Networking Event, The National Institute for Bioprocessing Research and Training, Belfield Campus, Dublin, October 2011

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“Development of $TiO_2$ composites for the removal of pesticides from water and wastewater using photocatalysis” R. O’ Dwyer, K. Nolan A. Morrissey, Ireland’s Environment 2012: EPA-STRIVE Research Conference -Environment & Human Health Challenges for Ireland, Trinity College Dublin, June 2012

“Development of $TiO_2$ composites for the removal of pesticides from water using photocatalysis” R. O’ Dwyer, K. Nolan A. Morrissey, Green Chemistry in Ireland II at Dublin City University 12th July 2012

“Development of Titanium Dioxide composites for the removal of pesticides from water using photocatalysis” R. O’ Dwyer, K. Nolan A. Morrissey, 7th European Conference on Pesticides and Related Organic Micropollutants in the Environment, Porto, Portugal, October 2012

“Development of Titanium Dioxide composites for the removal of pesticides from water using photocatalysis” R. O’ Dwyer, K. Nolan A. Morrissey, , School of Biotechnology, Dublin City University, Dublin, Ireland, January 2013

## *Oral Presentations*

**“**Development of novel adsorbents for the removal of selected endocrine disrupting compounds (EDCs) from water and wastewater” R. O’ Dwyer, J. Tobin, K. Nolan A. Morrissey. DCU Questor internal workshop, Dublin City University, Dublin, Feb 2010

“Development of novel photosensitisers for the removal of selected Endocrine disrupting compounds from water and wastewater using photocatalysis” R. O’ Dwyer, J. Tobin, K. Nolan A. Morrissey, 21st Irish Environmental Researchers’ Colloquium, University College Cork, April 2011

“Development of Titanium Dioxide composites for the removal of pesticides from water and wastewater using photocatalysis” R. O’ Dwyer, J. Tobin, K. Nolan A. Morrissey, School of Biotechnology 4th Annual Research Day, Dublin City University, Dublin, Jan 2012

“Development of Titanium Dioxide composites for the removal of pesticides from water and wastewater using photocatalysis” R. O’ Dwyer, J. Tobin, K. Nolan A. Morrissey, DCU Questor internal workshop, Dublin City University, Dublin, Feb 2012

“Development of Titanium Dioxide composites for the removal of pesticides from water and wastewater using photocatalysis” R. O’ Dwyer, J. Tobin, K. Nolan A. Morrissey, 22nd Irish Environmental Researchers’ Colloquium, University College Dublin, March 2012

“Development of Titanium Dioxide composites for the removal of pesticides from water using photocatalysis” R. O’ Dwyer, J. Tobin, K. Nolan A. Morrissey, IWA World Congress on Water ,Climate Change and Energy, The Convention Centre, Dublin, May 2012

“Development of Titanium Dioxide composites for the removal of pesticides from water using photocatalysis” R. O’ Dwyer, K. Nolan A. Morrissey, Canada-EU Partnership meeting, Laval University, Quebec, Canada, September 2012

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# List of symbols and abbreviations

2,4-D - 2,4-Dichlorophenoxyacetic acid
$\beta$ - Redlich and Peterson isotherm constant
AC - Activated carbon
AOP - Advanced oxidation process
C - Concentration (at specific t (time))
$C_i$ - Concentration initial
$C_f$ - Concentration final (after a given length of time)
C0 - Concentration at t = 0
CVD - Chemical vapour deposition
DDT - dichlorodiphenyltrichloroethane
DMF - Dimethylformamide
$e^-$ - electron
EC - European commission
EDC - Endocrine disrupting compounds
EDP - Endocrine disrupting pesticide
EDX - Energy dispersive X-ray
$E_G$ - Energy Gap
EPA - Environmental protection agency
FT-IR - Fourier transform infrared
GAC - Granular activated carbon
$h^+$ - positive hole
HPLC - High performance liquid chromatography
IPCA - Integrated photocatalytic adsorbent
IUPAC - International union of pure and applied chemistry
kapp - Apparent pseudo first-order rate constant
$K_F$ - Freundlich isotherm constant, l/g
$K_L$ - Langmuir isotherm equilibrium binding constant, l/mg
LC-MS - Liquid chromatography tandem mass spectrometry
LOD - Limit of detection (HPLC)
Log $P_{ow}$ - Log partition coefficient octanol water
LOQ - Limit of quantitation (HPLC)
m - Number of experimental data points
MCL - Maximum contaminant level
MCPA - 4- chloro-2methylphenoxyacetic acid
min - Minute
n - Exponent in Freundlich isotherm
NOM - Natural organic material
p - Number of parameters in the sorption isotherm
P25 -AEROXIDE® P25
PAC - Powdered activated carbon
$pK_a$ - Acid dissociation constant
PZC - Point of zero charge
q - Adsorption loading
$q_f$ - Adsorption final

$q_t$ - Adsorption at a given time
qm: - Maximum sorption capacity, mg/g
$R^2$ - Correlation coefficient
RMSE - Root mean squared error
S - Substrate
$S_0$ - Ground state
$S_1$ - Singlet state
SD - Standard deviation
SE - Standard error
SEM - Scanning electron microscope
SSE - Sum of squares error
t - Time
$T_1$ - Triplet state
$T_{½}$ - Half life
TCPP - 5, 10, 15, 20-Tetrakis-(4-carboxyphenyl)-21,23H-porphyrin
TEM - Transmission electron microscope
TOC - Total organic carbon
USEPA - United States Environmental Protection Agency
UV - Ultra violet (Light)
UV-Vis - Ultraviolet visible light
Wt. - Weight
XRD - X-ray diffraction

# 1 Scope of work

## 1.1 Introduction

Pesticides enter the aquatic environment through agricultural runoff, during strong rainfall events and may also enter water bodies through accidental spills and wastewater discharges (McGarrigle, Lucy and O'Cinneide 2010). The umbrella term "pesticides "refers to a large group of substances which are developed to mimic, and therefore substitute for specific molecules in targeted biological processes i.e. the pesticide mode of action is unique to the targeted pest (Gavrilescu 2005).

Poor quality water has been listed as one the major environment-related health threats in Europe (European Environment Agency 2011a) and pesticide pollution can be a significant contributor to poor water quality. Pesticides have harmful effects on non-target organisms such as humans, animals and the environment, have a range of toxic effects including carcinogenicity (Mathur *et al.* 2002) and can have endocrine disrupting capabilities (McKinlay *et al.* 2008).

Pesticides are widely used and detected across Europe in freshwater. In Ireland pesticides have been detected above the EU parametric limit set for them on a number of occasions (McGarrigle, Lucy and O'Cinneide 2010). In Europe freshwaters in the UK were found to be susceptible to pesticide pollution and in Germany groundwater was particularly affected by pesticide pollution (European Environment Agency 2011b).

The European Commission has put a range of legislation in place to prevent or minimise pesticide pollution, such as the Water Framework Directive (EC. 2000), the strategy for the control of endocrine disrupting compounds (EC 1999) and the Stockholm convention (EC. 2004b).

Conventional water treatment facilities do not efficiently removal pesticides from freshwater (Gibs *et al*. 2007), so alternative methods need to be investigated. To date the most effective pesticide removal techniques are adsorption and photocatalysis (Devipriya and Yesodharan 2005, Ahmad *et al*. 2010). The most commonly used adsorption technique is use of activated carbon.

Activated carbon has been widely adopted as a pesticide removal technique but it does have a recyclability issue (Ahmad *et al*. 2010). Pesticide removal by activated carbon is efficient but the problem of how to remove and treat the solid waste and pesticides trapped in its pores, in a cost effective manner, is still an issue that has to be dealt with.

Photodegradation as a removal technique for pesticide has been shown to work effectively (Autin *et al*. 2013). Photolysis using solar light, while effective, takes considerably more time when compared to UV light. Pesticides by their design are photo stable so high intensity lamps are required and this increases energy consumption and operating costs. The incorporation of a catalyst (photocatalysis) improves the efficiency of the removal technique. The most commonly used catalyst is Titanium Dioxide ($TiO_{2)}$. It is relatively cheap and easy to source (Fujino and Matzuda 2006). The drawback to this technique is again the energy consumption required for the UV lamps but solar photocatalysis poses an alternative to this. However solar photocatalysis is not viable in every country due to local weather conditions.

This PhD study investigates the use of the catalyst, titanium dioxide as a composite, with a variety of adsorbents, for the removal the of pesticides 2,4-Dichlorophenoxy acetic acid (2,4-D) and 4-Chloro-2-Methyl phenoxy acetic acid (MCPA) from water. The study combines the use of both adsorption and photocatalysis to physically trap and then photodegrade the pesticide. 2,4-D and MCPA are commonly applied pesticides in both Ireland and the EU and have been shown to exceed limits set by the EU and were therefore selected as target analytes for this study. Three separate $TiO_2$ composites were investigated in this study and are outlined in Figure 1-1 below.

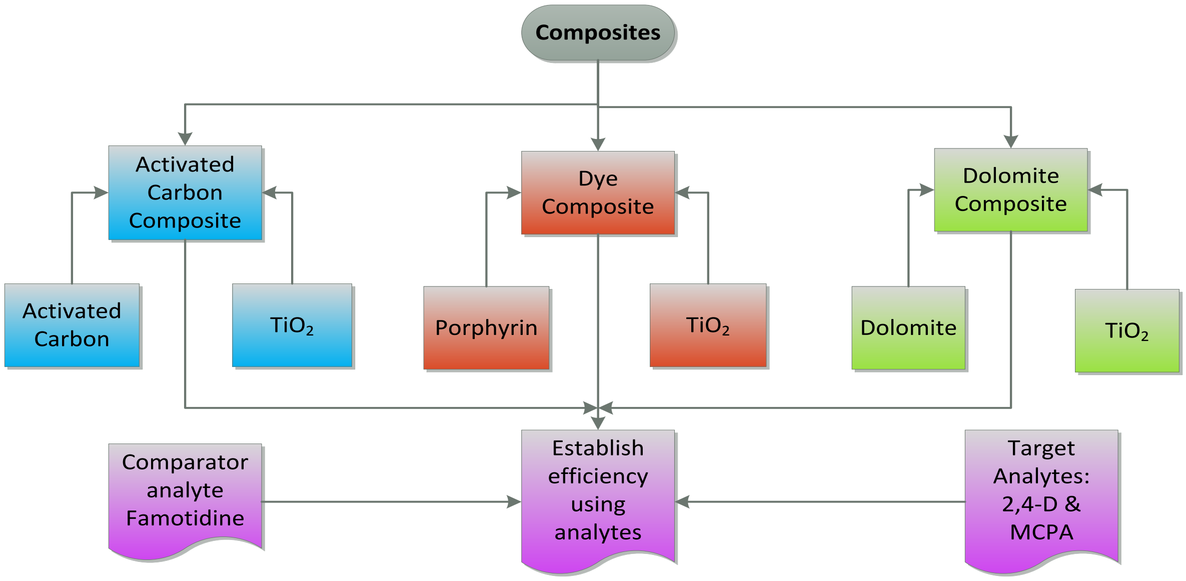

**Figure 1-1: Project flowchart showing three $TiO_2$ composites**

## 1.2 Aims and objectives

The main aim of this project is to investigate the removal and/or degradation efficiencies of 2,4-D and MCPA from water using $TiO_2$ composites under UV or visible light.

In order to achieve this aim, the following objectives were set:

1. Synthesising three types of composites; Activated carbon/$TiO_2$, dye/$TiO_2$ composites and dolomite/$TiO_2$ composites

2. Conducting adsorption studies, including baseline studies of selected pesticide adsorption, onto activated carbon, dolomite, $TiO_2$ and AC/$TiO_2$ composite

3. Undertaking photodegradation studies using visible & UV light to investigate the photocatalytic degradation of target analytes in $TiO_2$ slurries and with synthesised composites

4. Characterisation of produced composite with respect to microstructure and the associated physical properties

5. Analysing $TiO_2$ photocatalysis using mass spectrometry to determine target analyte degradation efficiencies.

## 1.3 Thesis layout

This thesis is divided into seven chapters. In this first chapter, an overview of the research is given. Chapter 2, then, sets the context for the following chapters by providing an insight into the available literature. The prevalence of pesticides in drinking water supplies in Ireland and Europe and the regulations and policy on the control of pesticides are discussed in this chapter as well as some commonly applied pesticides and their characteristics. The environmental distribution and health effects as well the fate of pesticides in current water treatment are examined. The primary focus of this chapter is a literature review of pesticide removal studies to be used as a benchmark and inform the current study.

Chapter 3 describes the methods utilised for investigating the different lines of research. Details of the adsorption studies are described, together with the details on the photocatalysis studies. The various analytical detection methods are also described along with sample preparation.

Chapter 4 focuses on the Activated Carbon/Titanium Dioxide (AC/$TiO_2$) composite. The preparation, characterisation and adsorption of the composite with the target analytes are examined. Optimisation parameters for the efficient removal of pesticides are discussed along with the adsorption and photocatalysis function of the composites. Adsorption modelling is also investigated in chapter 4.

Chapter 5 discusses the results of the dye/$TiO_2$ composite removal and dolomite/$TiO_2$ composite. The composite preparation and characterisation are evaluated together with the removal efficiency of the target analytes. The removal efficiency is compared with that of other analytes and discussed.

Chapter 6 focuses on $TiO_2$ photocatalysis in more detail and compares the findings of this study to the current available literature. Mass spectra are examined as well as the addition of hydrogen peroxide to the system.

Finally chapter 7 concludes the work by identifying the overall conclusion and contributions of this work as well as recommending suggestions for further study.

# 2 Literature Review: Removal of Pesticides from drinking water supplies

## 2.1 Introduction

Poor quality water has been listed as one the major environment-related health threats in Europe and the US, for a number of years, and continues to be a threat (European Environment Agency 2011a). Industrial chemistry has developed and continues to develop a vast range of synthetic chemicals such as pesticides, plastics and pharmaceuticals. These chemicals and their breakdown products can be introduced to wastewater streams and potentially into drinking water from manufacturing effluent streams and from the ultimate use of the chemicals (European Environment Agency 2011b). An overview of the prevalence of pesticides in Europe, as well as a description of the relevant pesticide legislation is provided. In addition some commonly applied pesticides and their characteristics as well as their environmental distribution and the health effects that they cause are examined, with a particular emphasis on the removal of pesticides from water supplies.

Pesticides mainly enter the aquatic environment through agricultural runoff during strong rainfall events (European Environment Agency 2011b). In addition they may enter water bodies through accidental spills and wastewater discharges (McGarrigle, Lucy and O'Cinneide 2010). Pesticide pollution depends on a number of factors (European Environment Agency 2011b) including:

- Chemical nature of the pesticide
- Physical properties of the landscape
- Weather conditions

Pesticides can be classified by the target organism (e.g. herbicides, insecticides, fungicides and rodenticides). Pesticide structures are developed to mimic, and therefore substitute for specific molecules in targeted biological processes i.e. the pesticide mode of action is unique to the targeted pest (Gavrilescu 2005). Pesticides can however have harmful effects to non-target organisms such as humans, animals and the environment and have a range of toxic effects that may be carcinogenic

(Mathur *et al*. 2002) and have endocrine disrupting capabilities (McKinlay *et al.* 2008).

Regulators work on the basis of identifying hazardous pesticides and either banning these or restricting their use. For example the department of Agriculture Food and Marine published a report on the sustainable use of pesticides in Ireland (D.A.F.M. 2013). The plan defines a national strategy to achieve a sustainable use of pesticides and sets down objectives, quantifiable measures and timeframes to reduce the risks associated with the use of pesticides. This is a requirement under Directive 2009/128/EC (EC. 2009) of the European Parliament establishing a framework for Community action to achieve the sustainable use of pesticides.

However, as long as pesticides continued to be used in agriculture, a certain proportion will reach natural water systems, i.e., via surface runoff during strong rainfall events (Schulz 2004) and therefore developing methods for their removal from water supplies continues to be of importance.

## 2.2 Prevalence of pesticides in drinking water supplies in Ireland and Europe

### Ireland

It is difficult to obtain data on the prevalence of pesticides in the environment. Pesticides are a diverse group of chemicals, each requiring an analytical test method specific for that pesticide or group of pesticides and often require sophisticated test methods with labour intensive extraction steps as well as derivitisation to detect low levels of the pesticide (Herrero-Hernández *et al.* 2013). Pesticides and total pesticides are included in the chemical parameters for testing drinking water but “only those pesticides which are likely to be present in a given supply are required to be monitored” according to the European Communities (Drinking Water) (No. 2) Regulations 2007 (Irish Government. 2007). The list of pesticides to be screened for is determined by the relevant water supply authority. As a result, wastewater treatment and water treatment plants do not routinely test for all pesticides, which mean that data is limited.

In 2011, 1,442 samples were analysed in Ireland for pesticides in 925 water supplies. The most recent EPA report on the provision and quality of drinking water in Ireland demonstrates that some individual pesticides are being detected above their EU recommended maximum limit (parametric value) of 0.1 µg/l (Hayes *et al.* 2012). However, the total pesticides parameter for this reporting period did not exceed its parametric value of 0.5 µg/l. Of the pesticides that exceeded their parametric values over the last three years, the most commonly detected were MCPA, Isoproturon, Mecoprop, 2,4-D, Atrazine and Simazine. Irish EPA reports conclude that conventional water treatment facilities are not consistently capable of removing pesticides below recommended limits in water supplies.

### Europe

Pesticides are widely used and detected across Europe in freshwater. They are often transported by diffuse pathways from surface run off (European Environment Agency 2011b). In terms of surface water the European Environment Agency (EEA) found that a proportion of UK freshwater bodies were at risk from diffuse pollution by agricultural pesticides. In general groundwater was observed to exceed the threshold of pesticides although declining trends were evident in Germany, where 4 % of groundwater bodies exceed the quality standard from diffuse pollution of pesticides (Arle *et al.* 2010).

In a large-scale sampling and monitoring programme of 60 organic compounds of both river and groundwater organised by The Joint Research Centre[1], (Loos *et al.* 2009), pesticides were generally found at relatively low concentrations. However, these low values could be accounted for by the fact that the study was conducted in autumn which is an uncommon application period for pesticides. On the other hand, relatively high average concentrations of Isoproturon were found at 2 µg/L which is 85 % above the legal limit allowed.

As previously mentioned, data on pesticide usage throughout the EU is limited. It is therefore difficult to predict the prevalence of specific pesticides in water supplies in member states. Directive 2009/128/EC (EC. 2009) on the sustainable use of pesticides set out a requirement for all member states to report pesticide usage. This will help improve the availability of data.

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[1] The Joint Research Centre is the European Commission’s in-house science service

## 2.3 Regulations & Policy on the Control of Pesticides

### 2.3.1 Water Framework Directive

The Water Framework Directive sets environmental objectives of good chemical status for surface waters and for the prevention of pollution of groundwater (EC. 2000). Annex VIII of the directive provides an indicative list of the main pollutant types in water systems, where specific reference is made to "biocides and plant protection products" (EC. 2000). In Annex X of the directive lists priority substances in water policy, which includes a number or pesticides: Atrazine, Alachlor, Chlorfenvinphos, Chlorpyrifos, Diuron, Endosulfan, Isoproturon, Pentachlorophenol, Simazine and Trifluralin. This list was been updated in Annex II of Directive 2008/105/EC on environmental quality standards in the field of water policy. The pesticides on the list have not changed (EC. 2008). Atrazine has been banned and Simazine has been withdrawn from the EU with "essential use" derogations since 2004 (EC. 2004a). Endosulfan had been banned in the EU since 2005 (EC. 2005). Although these pesticides have been banned they are still being detected in Irish surface waters (EPA 2006) due to their persistence.

### 2.3.2 EU Endocrine Disrupting Chemicals Strategy

An emerging area of concern is the presence of endocrine disrupting chemicals (EDCs) in drinking water supplies. An endocrine-disrupting compound is defined by the European Commission as *"an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations"*(EC 2011).

In 1999 the European Commission set out a strategy for the control of EDCs (EC 1999). One of the main objectives was the establishment of a priority list of chemicals for evaluation of their role in endocrine disruption. This list was published in 2000 and contained 553 synthetic chemicals and 9 synthetic/natural hormones.

The most recent review in 2007 indicates that to date 575 chemicals were evaluated and 320 remained on the EDC list (EC 2007). This report specifically mentioned organophosphor pesticides, Omethoate and Quinalphos as well as the pesticides Chlordimeform, Trifluralin and Ethylene thiourea as being substances with evidence of endocrine disrupting (ED) effects (Category 1), which are already regulated or being addressed under existing legislation. Dimephenthoate is listed as a substance with potential evidence of ED effects (Category 2), which is already regulated or being addressed under existing legislation (EC 2007). 2,4-D is a suspected endocrine disruptor and its endocrine disrupting activity is being tested (US EPA  2011). Pesticides with endocrine disrupting capabilities are discussed further in section 2.6.3.

As additional studies on pesticides with ED potential are identified, a more accurate list of EDCs will emerge as well as more regulation and control of use of these (EC 2011).

### 2.3.3 Other EU legislation

The Stockholm convention on persistent organic pollutants (POPs) forms a framework, based on the precautionary principle, which aims to guarantee the safe elimination of those substances, which are harmful to human health and the environment, as well as reductions in their production and use (EC. 2004b). Persistent organic pollutants are defined by the convention as "*chemical substances that possess certain toxic properties and, unlike other pollutants, resist degradation*". POPs are particularly harmful for human health and the environment (EC. 2004b). The convention covers 18 priority POPs of which 12 are pesticides. (UN Economic and Social Council 2009).

There are a number of other pieces of EU legislation that relate to pesticides. Regulation 283/2013 (EC. 2013) sets out the data requirements for active substances that need to be submitted to the EU before placing them on the market. The data is mainly environmental and safety data. There is also a regulation on the marketing of pesticides (Regulation 1107/2009), which lays out the information that needs to be in place before a pesticide is released into the market. The EU is also trying to promote the sustainable use of pesticides by introducing Directive 2009/128/EC establishing community action to achieve the sustainable use of pesticides (EC. 2009), which aims at reducing the risks and impacts of pesticide use on human health and the environment and promoting the use of integrated pest management and of alternative approaches or techniques such as non-chemical alternatives to pesticides.

## 2.4 Commonly applied Pesticides usage and characteristics

### Ireland

In 2003 the department of agriculture in Ireland published a pesticide usage survey on grassland and fodder crops (Pesticide Control Service 2003). This is the most up to date survey available for Ireland at the time of writing. A summary of the most commonly applied pesticides from the survey is shown below in Table 2-1, where it can be seen that MCPA was the most commonly applied.

**Table 2-1: Pesticide usage in grassland and fodder crops in Ireland 2003**

| Rank | Pesticide (Active) | Total kg applied 2003 |
|---|---|---|
| 1 | MCPA | 221,883 |
| 2 | Glyphosate | 93,056 |
| 3 | Mecoprop-P | 74,598 |
| 4 | Atrazine | 24,152 |
| 5 | 2,4-D | 23,458 |

### Europe

It is estimated that EU countries applied 2,732,216 tonnes of active substances (pesticides) from 1992-2003 (Muthann and Nadin 2007). This corresponds to 2.1 kg of active substance per hectare. The country that applied the most pesticides was France with a peak of 89,084 tonnes in the year 2000. Fungicides were the mostly commonly applied type of pesticide in the EU, followed by herbicides and then insecticides. The top five fungicides, herbicides and insecticides applied in the EU are shown below in Table 2-2.

**Table 2-2: Summary of Eurostat findings on use of pesticides in EU** (Muthann and Nadin 2007)

| Rank | Active Substance | Quantity applied 2003 (tonnes) |
|---|---|---|
| | | *fungicides* |
| 1 | Sulphur | 59053 |

| | | |
|---|---|---|
| 2 | Mancozeb | 15946 |
| 3 | Fosetyl | C |
| 4 | Metiram | 2798 |
| 5 | Folpet | 1418 |
| | *herbicides* | |
| 1 | Glyphosate | C |
| 2 | Isoproturon | 12073 |
| 3 | MCPA | 5293 |
| 4 | Pendimethalin | 3141 |
| 5 | 2,4-D | C |
| | *insecticides* | |
| 1 | chlorpyrifos | 1226 |
| 2 | Parathion-methyl | C |
| 3 | Dimethoate | 581 |
| 4 | Imidacloprid | C |
| 5 | Methomyl | 398 |

C= confidential information therefore no value is given

## Characteristics of selected commonly used pesticides

There are over 1,200 pesticides on the market in the EU (EU 2013). This section of the review describes in more detail the pesticides that are most commonly used in the EU and in Ireland.

## MCPA

The pesticide MCPA is another chlorophenoxy acid compound that is a selective systemic hormone type herbicide absorbed by leaves and roots. MCPA is used to control a wide range of broadleaf weed for cereals, grassland, and turf.

MCPA acid is practically insoluble in water, non-volatile and somewhat lipophilic. MCPA is mentioned as important in the WHO Guidelines for Drinking-water Quality and was found to have had a photolytic half-life of 20–24 days in sunlight (World Health Organisation 2003). MCPA has limited evidence of carcinogenicity (IARC 1991a)[2] and is “moderately toxic” to “practically non-toxic” to birds (USEPA 2005). In general, toxicity tests indicate MCPA is “slightly toxic” to mammals exposed for short periods based on data submitted for MCPA acid. It is classed as highly toxic’ to ‘moderately toxic’ to freshwater fish exposed for short periods of time.

As shown in Table 2-1 MCPA was the most commonly applied Pesticide in Ireland in 2003. In Europe it was the third most commonly applied herbicide Table

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[2] International Agency for Research on Cancer

2-2 and in the US approximately 4.6 million pounds ($2.087 \times 10^{6}$ kg) of MCPA active ingredient are applied annually to approximately 12 million acres (USEPA 2005).

### Glyphosate

Glyphosate is a non-selective herbicide that is the active ingredient in “Roundup” weed killer produced by Monsanto and is among the most widely used pesticides by volume in the world (Baylis 2000). In Ireland it is the second most commonly applied pesticide on grassland and fodder crops (Table 2-1) and the most commonly applied herbicide in Europe (Table 2-2). In the US Glyphosate ranks number one as the most commonly used conventional pesticide (2001-2007) in the agricultural market sector and the second most commonly used in the home and garden market sector (IARC 1987)

Glyphosate is highly water soluble and also adsorbs strongly to soil. It appears that it has a low potential to move to ground-water due to strong adsorptive characteristics to soil demonstrated in laboratory and field studies. However, glyphosate does have the potential to contaminate surface waters due to its aquatic use patterns and erosion via transport of residues adsorbed to soil particles suspended in runoff water (Borggaard and Gimsing 2008). If glyphosate was to reach surface waters it would be resistant to hydrolysis and aqueous photolysis. It was found to be stable to photodegradation in pH 5, 7, and 9 buffered solutions under natural sunlight (US EPA 1994). Glyphosate has the potential to cause kidney damage and reproductive effects from long-term exposures. Recently the US EPA has raised the permitted tolerance levels of glyphosate residue in many of the fruits and vegetables (US EPA. 2013).

The European Commission reviewed the use of glyphosate as a herbicide in 2001 and laid down a number of provisions on its use (EC 2001b). In particular it stated that particular attention must be paid to “the protection of the groundwater, in vulnerable areas, in particular with respect to non-crop use.

### Mecoprop-P

Mecoprop-p is a member of the chlorophenoxy class of herbicides used on annual and perennial broadleaf weeds (USEPA 2007). Although it is the third most commonly applied pesticide on grassland crops in Ireland (Table 2-1) it does not appear in the top ten list of use of pesticides used in EU but is the third most commonly used pesticide in the EU on Cereal crops (Muthann and Nadin 2007).

Mecoprop-p is highly water soluble and does not sorb appreciably to soil constituents so can easily leach into both groundwater and surface water (Mottier et al. 2014). Mecoprop-p had been found in EU water treatment effluent at a maximum concentration of 2209 ng/L (Loos *et al.* 2009). Mecoprop-p is classified by the USEPA as slightly toxic (USEPA 2007).

### Atrazine

Atrazine is a triazine herbicide that is one of the most widely used herbicides in the world (EC. 2001). Although it has been banned in the EU since 2004, it is still in use in the US and is currently under review by the US EPA (US EPA 2011). It is included in the EC list of priority substances (EC. 2001), has relatively high solubility in water (1.61 x $10^{-4}$ mg/L) and is persistent in the environment (Camel and Bermond 1998). Atrazine is not readily biodegradable and is an endocrine-disrupting pesticide with a half-life of days to years, depending on the environment in which it is present. In Ireland the Environmental Protection Agency has stated that the annual average concentration of Atrazine in surface waters is 0.6µg/l (EPA 2006). This demonstrates that Atrazine is still persistent in Irish waters despite its ban.

### 2,4-D

The pesticide 2,4-D is a chlorophenoxy acid and is widely used as a broadleaf herbicide. Its relative stability and photostability in natural waters indicates that it is a persistent pesticide in the environment (Trillas, Peral and Domènech 1995). The US EPA has set a maximum contaminant level (MCL) for 2,4-D in drinking water at 0.07 mg/L or 70 ppb (US EPA 2011). The European Commission reviewed the use of 2,4-D as a herbicide in 2001 (EC 2001a) and laid down a number of provisions on its use. In particular it stated that particular attention must be paid to “the protection of the groundwater, when the active substance is applied in regions with vulnerable soil and/or climatic conditions”. The half-lives of 2,4-D in water range from 1 to several weeks under aerobic conditions and can exceed 120 days under anaerobic conditions (US EPA  2011,). It also possess high solubility in water (23180 mg/l at pH7 unbuffered)

2,4-D exhibits low to slight acute toxicity with the exception of the acid and salt forms which are severe eye irritants. The esters range from highly to slightly toxic to marine or freshwater fish. It is classified as moderately toxic to practically non-toxic to birds on an acute oral basis. There is concern regarding its endocrine disruption potential based on currently available toxicity data (McKinlay *et al.* 2008), which demonstrate effects on the thyroid and gonads following exposure to 2,4-D.

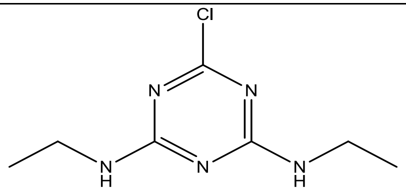
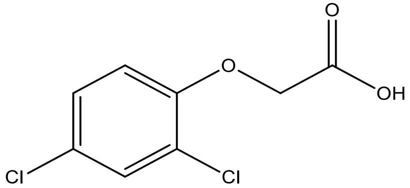
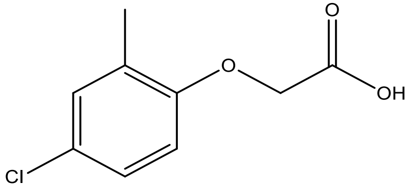
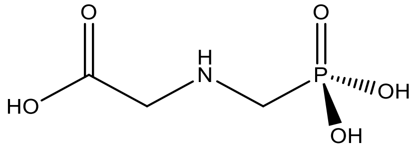
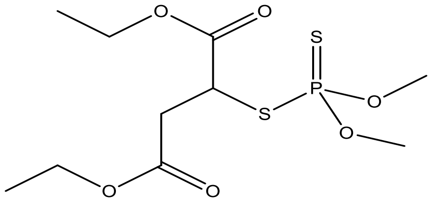
From Table 2-1 it can be seen that 2,4-D was the 5th most commonly applied pesticide in Ireland. It is also the 5th most commonly applied herbicide in Europe (Table 2-2). The US EPA estimated that between 1993 and 2000 the total annual domestic usage of 2,4-D was approximately 46 million pounds ($2.087x10^7$ kg), with 30 million pounds ($1.36x10^7$ kg)  (66 %) used for agriculture and 16 million pounds ($7.26x10^6$) (34 %) used for non-agriculture (US EPA  2011).

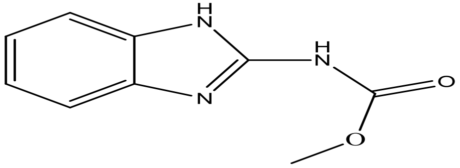
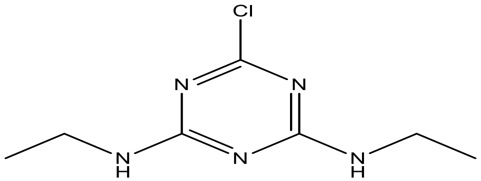
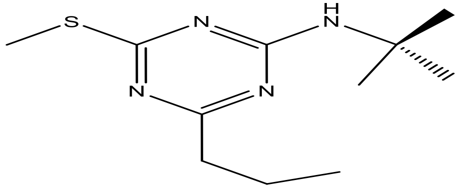
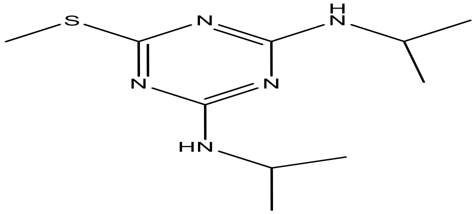
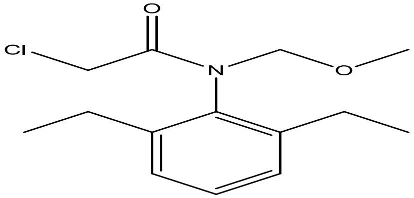
The physiochemical properties (Table 2-3) and the structures (Table 2-4) of the aforementioned pesticides are shown below as well as some other commonly applied pesticides.

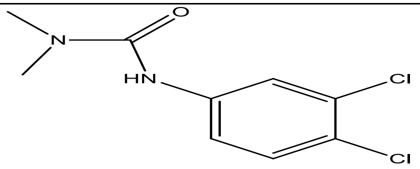
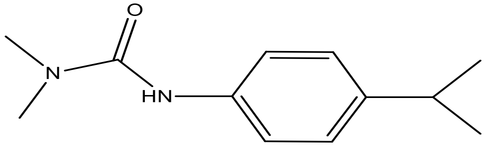
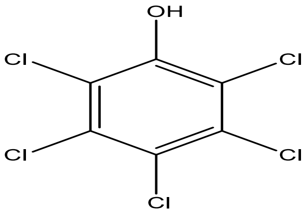
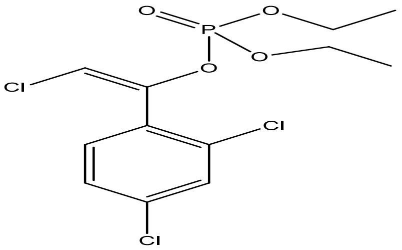
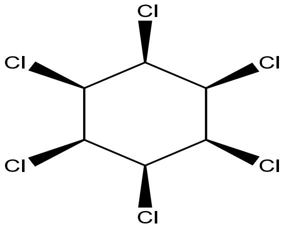
**Table 2-3: Physiochemical properties of selected pesticides** (Tomlin 1994)

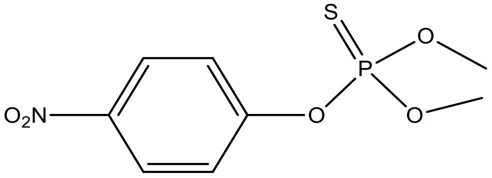
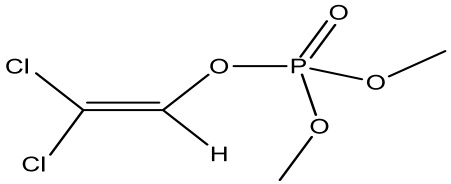
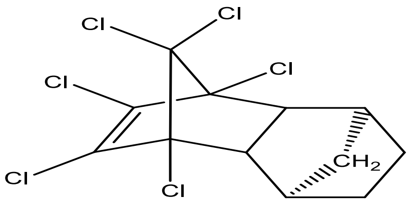
| Pesticide | Molecular weight (g/mol) | Water solubility (mg/L) | logK$_{ow}$ | PK$_a$ |
|---|---|---|---|---|
| Atrazine | 215.7 | 33 (20$^{0}$C) | 2.5 (25$^{0}$C) | 1.7 |
| 2,4-D | 221.0 | 311 pH1 , (25$^{0}$C) | 2.58-2.83 | 2.64 |
| MCPA | 200.6 | 734 (25°C pH1) | 2.75 (pH1)0.46 (pH5) 25$^{o}$C | 3.07 |
| Glyphosate | 169 | 10500 (20°C) pH 2 | 3.2 (25 °C) pH5-9 | 10.2 (25 °C) |
| Malathion | 330.4g/mol | 145 mg/l (20-25$^{0}$C) | log Pow: 2.75 | |
| Carbendazim | 191.2 | 29 (pH4), 8 (pH7), 7 (pH8)-24$^{0}$C | 24 (pH5), 32(pH7) 31 (pH9) | 4.2 |
| Simazine | 201.7 | 6.2 (20$^{0}$C) | 2.1 (25$^{0}$C) | PK$_b$12.3 |
| Terbutryn | 241.4 | 22 (20$^{0}$C) | 3.65 (25$^{0}$C) | PK$_b$ 9.7 |
| Prometryn | 241.4 | 33 (25$^{0}$C) | 3.1 (25$^{0}$C) | 4.1 |
| Isoproturon | 206.3 | 65 (22$^{0}$C) | 2.5 (pH7, 22$^{0}$C) | |
| Diuron | 233.1 | 42 (25$^{0}$C) | 700 ± 50 (25$^{0}$C) | |
| Alachlor | 269.8 | 242 (25$^{0}$C) | 3.52 | 0.62 |
| Pentachlorophenol | 266.3 | 80 (30$^{0}$C) | -3.77 | 4.71 |
| Chlorfevinphos | 359.6 | 145 (23$^{0}$C) | 3.85 | |
| Lindane | 290.8 | 7.3 (25$^{0}$C), 12 (35$^{0}$C) | 3.20-3.89 | |
| Methyl Parathion | 263.2 | 55 (20$^{0}$C) | 3.0 | |
| Dichlorvos | 221.0 | 8 (25$^{0}$C) | 1.9 | |
| Aldrin | 364.9 | Insoluble | 6.5 | |

**Table 2-4: Chemical names and structures of selected pesticides**

| Name | IUPAC name | Chemical Formula | Structure |
|---|---|---|---|
| Atrazine | 6-chloro-*N*$^2$-ethyl-*N*$^4$-isopropyl-1,3,5-triazine-2,4-diamine | $C_8H_{14}ClN_5$ |  |
| 2,4-D | (2,4-dichlorophenoxy)acetic acid | $C_8H_6Cl_2O_3$ |  |
| MCPA | 4-chloro-o-tolyoxyacetic acid | $C_9H_9ClO_3$ |  |
| Glyphosate | N-(phosphonomethyl)-glycin | $C_3H_8NO_5P$ |  |
| Malathion | diethyl (dimethoxyphosphinothioylthio) succinate | $C_{10}H_{19}O_6PS_2$ |  |

| **Name** | **IUPAC name** | **Chemical Formula** | **Structure** |
|---|---|---|---|
| Carbendazim | methyl benzimidazol-2-ylcarbamate | $C_9H_9N_3O_2$ |  |
| Simazine | 6-chloro-*N*$^2$,*N*$^4$-diethyl-1,3,5-triazine-2,4-diamine | $C_7H_{12}ClN_5$ |  |
| Terbutryn | *N*$^2$-*tert*-butyl-*N*$^4$-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine | $C_{10}H_{19}N_5S$ |  |
| Prometryn | *N*$^2$,*N*$^4$-diisopropyl-6-methylthio-1,3,5-triazine-2,4-diamine | $C_{10}H_{19}N_5S$ |  |
| Isoproturon | 3-(4-isopropylphenyl)-1,1-dimethylurea | $C_{12}H_{18}N_2O$ |  |

| **Name** | **IUPAC name** | **Chemical Formula** | **Structure** |
|---|---|---|---|
| Diuron | 3-(3,4-dichlorophenyl)-1,1-dimethylurea | $C_9H_{10}Cl_2N_2O$ |  |
| Alachlor | 2-chloro-2′,6′-diethyl-*N*-methoxymethylacetanilide | $C_{14}H_{20}ClNO_2$ |  |
| Pentachlorophenol | pentachlorophenol | $C_6HCl_5O$ |  |
| Chlorfevinphos | (*EZ*)-2-chloro-1-(2,4-dichlorophenyl)vinyl diethyl phosphate | $C_{12}H_{14}Cl_3O_4P$ |  |
| Lindane | 1α,2α,3β,4α,5α,6β-hexachlorocyclohexane | $C_6H_6Cl_6$ |  |

| Name | IUPAC name | Chemical Formula | Structure |
|---|---|---|---|
| Methyl parathion | *O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate | $C_8H_{10}NO_5PS$ |  |
| Dichlorvos | 2,2-dichlorovinyl dimethyl phosphate | $C_4H_7Cl_2O_4P$ |  |
| Aldrin | (1*R*,4*S*,4a*S*,5*S*,8*R*,8a*R*)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene | $C_{12}H_8Cl_6$ |  |

## 2.5 Environmental distribution of pesticides

Pesticide-related pollution is a persistent environmental problem (de Jong, de Snoo and van de Zande 2008, De Schampheleire *et al.* 2007). Pesticides pose potential risks to air and water quality, crops, animal health, and human health. Significant issues related to pesticide use and application, include over-application, contamination of surface and ground water (Reichenberger *et al.* 2007) and drift to unintended targets.

Pesticide drift is defined as the amount of pesticide active ingredient that is deflected out of the treated area by the action of air currents (De Schampheleire *et al.* 2007). Large portions of applied pesticides fail to reach the target site altogether (Reimer and Prokopy 2012). Pesticide drift to non-target areas causes crop losses and damage to natural areas and wildlife populations (Pimentel *et al.* 1992). As previously mentioned in section 2.3.3 the EU have particular concerns about the dispersal of pesticides categorised as persistent organic pollutants (POPs). These POPs can be transported across international boundaries far from their sources, even to regions where they have never been used or produced (UN Economic and Social Council 2009).

## 2.6 Health effects on humans and wildlife

### 2.6.1. General toxicity

Toxicity can be measured in a number of ways. The World Health Organisation (Sheffer 2009) measures toxicity under the following headings;

- Toxicity to microorganisms
- Toxicity to aquatic organisms
- Toxicity to terrestrial organisms

WHO reports look at individual toxicity studies that have been conducted using the pesticides on target organisms (Sheffer 2009). Parameters such as $LC_{50}$ (the concentrations of the pesticide in the medium that kills 50 % of the test organism during the observation period), $LD_{50}$ (the amount of a pesticide, given all at once, which causes the death of 50 % of a group of test organisms) and physiochemical properties of the pesticides are taken into account. The data is then correlated and put into a scale. All of the studies on 2,4-D toxicity were correlated and the WHO classed 2,4-D as low to moderate toxicity to aquatic organisms (World Health Organisation 1989). The WHO has not correlated studies on MCPA toxicity but it was reported that kidney toxicity was observed in dogs that had been given high doses (1.5 mg/kg of body weight per day) of MCPA (World Health Organisation 2003).

Toxicity classing is limited by the number of studies and study limitations in published literature. For example there are “limited data on the effects of 2,4-D and its formulations on communities of organisms; hazard assessment is, therefore, often by extrapolation from single species studies” (World Health Organisation 1989). Table 2-5 shows the toxicity of selected pesticides classed by WHO.

## Table 2-5: WHO Toxicity classification of selected pesticides

| Pesticide | WHO toxicity to microorganisms | WHO toxicity to aquatic organisms | WHO toxicity to terresterial organisms |
|---|---|---|---|
| **2,4-D** | -inconclusive | -low to moderate | -low acute toxicity to birds |
| **Glyphosate** | -not possible to separate the toxic effects of the herbicide from changes in the habitat caused by herbicidal action | -slightly toxic to aquatic macrophytes<br>-moderately to very slightly toxic to fish | -low toxicity for bees and earthworms<br>-low toxicity to birds |
| **Carbendazim** | -inconclusive | -highly toxic to some aquatic organisms<br>-the most sensitive species: channel catfish | -low acute toxicity to laboratory mammals<br>- selective toxicity toxic to earthworms |
| **Pentachlorophenol** | -inconclusive | -high toxicity to fish | -highly toxic for birds |
| **Lindane** | -lethal to *Scenedesmus acutus* | -moderately toxic for invertebrates and fish | -acute oral toxicity of lindane is moderate |
| **Methyl Parathion** | -inconclusive | -highly toxic for aquatic invertebrates | -moderately toxic for birds |
| **Dichlorvos** | -little or no toxic effect on microorganisms degrading organic matter in sewage | -moderate to high acute toxicity for freshwater and estuarine species of fish | -slightly to moderately toxic for birds<br>highly toxic to bees |
| **Aldrin** | -inconclusive | -highly toxic for aquatic crustaceans and fish | -phytotoxic, to tomatoes and cucumbers |

### 2.6.2. Carcinogenic Pesticides

Pesticides can also have carcinogenic effects i.e can be capable of causing cancer (Alexander *et al.* 2011). The International Agency for Research on Cancer (IARC) is the specialised cancer agency of the World Health Organisation. The IARC publish monographs on the evaluation of carcinogenic risks to humans on regular basis with the most recent volume (100) being published in 2012 (IARC 2012). The aim is to publish critical reviews and evaluations of evidence on the carcinogenicity of a wide range of human exposures. Each Monograph reviews relevant epidemiological studies and cancer bioassays in experimental animals.

Carcinogenicity is classed by the IARC into one of five main groups;

Group 1: The agent is carcinogenic to humans

Group 2A: The agent is probably carcinogenic to humans

Group 2B: The agent is possibly carcinogenic to humans

Group 3: The agent is not classifiable as to its carcinogenicity to humans

Group 4: The agent is probably not carcinogenic to humans

A table showing selected pesticides and their corresponding carcinogenic group is shown below (Table 2-6).

**Table 2-6: IARC carcinogenicity rating of selected pesticides**

| Pesticide | Carcinogenic group | Reference |
|---|---|---|
| Atrazine | Group 3 | (IARC 1999a) |
| 2,4-D | Group 2B | (IARC 1999b) |
| MCPA | Group 2B | (IARC 1999b) |
| Malathion | Group 3 | (IARC 1991b) |
| Simazine | Group 3 | (IARC 1991b) |
| Pentachlorophenol | Group 2B | (IARC 1991b) |
| Lindane | Group 2B | (IARC 1999b) |
| Methyl Parathion | Group 3 | (IARC 1987) |
| Dichlorvos | Group 2B | (IARC 1991c) |
| Aldrin | Group 3 | (IARC 1987) |

### 2.6.3. Endocrine Disrupting Pesticides (EDPs)

Endocrine-disrupting activity has also been documented for certain pesticides (European Environment Agency 2011b). The impacts of endocrine disrupting pesticides (EDPs) on the environment and on health are as yet not fully understood and a direct causal relationship from low level exposure is difficult to prove. There is however an increasing consensus among international experts of an association between EDP exposure and negative health effects. *"The evidence for adverse reproductive outcomes (infertility, cancers, malformations) from exposure to endocrine disrupting chemicals is strong, and there is mounting evidence for effects on other endocrine systems, including thyroid, neuroendocrine, obesity and metabolism, and insulin and glucose homeostasis."* (Diamanti-Kandarkis *et al.* 2009)

Examples of pesticides that have endocrine disrupting capabilities are DDT, Endosulfan and Atrazine (EC 2007). These pesticides are highly restricted or banned completely (Pesticide Action Network Europe 2008). Alachlor and 2,4-D are other examples of endocrine disrupting herbicides. 2,4-D is a suspected endocrine disruptor that is repeatedly found in river bodies (Page *et al.* 2009) and its endocrine disrupting activity is being tested (US EPA 2011).

Examples of endocrine disrupting effects from pesticides include morphological abnormalities in male alligators in Lake Apopka in Florida exposed to organochlorine pesticides (Garrison *et al.* 2010), the demasculinisation of African clawed frogs (*Xenopus laevis)* exposed to Atrazine (Hayes *et al*. 2002) and endocrine disruption in feral carps (Cyprinus carpio) in the Ebro River (Spain) (Lavado *et al.* 2004). Reproductive effects in birds with exposure to EDPs have also been noted and discussed (Ottinger *et al*. 2005).

The three major biological effects of endocrine disruption are the mimicking or antagonising of the effects of hormones, the altering of synthesis patterns and metabolism of hormones and the modifying of hormone receptor levels (Diamanti-Kandarkis *et al.* 2009).

The US endocrine society highlight the fact that due to similar receptors and enzymes no endocrine system is immune from the effect of EDPs, that EDPs may accumulate in the food chain and the effects of endocrine disrupting chemicals may also be transmitted to future generations through the germline epigenetic modification or from continued exposure of offspring to the chemical (Diamanti-Kandarkis *et al.* 2009) .

It is difficult to conclusively show an effect from continuous exposure to lower levels of chemicals in the environment (EC 1999). This is a complex field of study as many factors need to be taken into account such as age of exposure, latency from exposure, the mixture of chemicals, dose-response dynamics and long term latent effects (Diamanti-Kandarkis *et al*. 2009).

Table 2-7 shows the biological effects of the selected pesticides.

**Table 2-7: Endocrine Disrupting (ED) Effects of selected pesticides** (McKinlay *et al.* 2008)

| Pesticide | ED Effects |
|---|---|
| Malathion | Inhibits catecholamine secretion, binds to thyroid hormone receptors. |
| Atrazine | Androgen inhibitor with a weak oestrogenic effect. Disrupts the hypothalamic control of lutenising hormone and prolactin levels. Induces aromatase activity, increasing oestrogen production. Damages the adrenal glands and impairs steroid hormone metabolism. |
| Carbendazim | Increases oestrogen production by increasing aromatase activity. |
| Simazine | Induces aromatase activity, increasing oestrogen production. |
| Diuron | Inhibits the actions of androgens. |
| Alachlor | Binds competitively to oestrogen and progesterone receptors. Interacts with the pregnane X cellular receptor, interfering with the manufacture of enzymes responsible for steroid hormone metabolism. |
| Pentachlorophenol | Weak oestrogen mimic and anti-androgen. |
| Chlorfenvinphos | Weak oestrogen mimic. |
| 2,4-D | Synergistic androgenic effects when combined with testosterone. |
| HCH (lindane) | Shortens oestrous cycles and lowers luteal progesterone concentrations. Increases the blood serum concentrations of insulin and oestradiol, decreases thyroxine concentrations. |
| Parathion | Inhibits catecholamine secretion, increases nocturnal synthesis of melatonin, causes gonadotrophic hormone inhibition. |
| Dichlorvos | Weak androgen-receptor antagonist. |
| Aldrin | Antagonises the action of androgens by binding competitively to their receptors and inhibiting the genetic transcription they induce. |

There have been a number of epidemiological studies that show the effect of EDPs on human health.

An increased rate of breast cancer has been detected in the female population in Jaipur (Mathur *et al.* 2002). The carcinogenic effect occurs only with high and sustained levels of exposure to pesticides. It was determined that the blood of females with breast cancer contained three times as much organochlorine pesticides[3] than normal females.

Birth defects have also been associated with exposure to endocrine disrupting pesticides [4] (Garry *et al.* 2002). The region study in Minnesota showed the highest age adjusted rate of birth defects when compared with urban areas of Minnesota. Personnel working as pesticide applicators in the region demonstrated even higher levels of age adjusted birth defect rates when compared to the general population.

The EDPs Endosulfan, Toxaphene, and Dieldrin were found to have estrogenic effects on human estrogen-sensitive cells (Soto, Chung and Sonnenschein 1994). Human breast cancer estrogen-sensitive MCF7 cells were used to determine estrogenic effects. Dieldrin and Toxaphene were found to be estrogenic at 10 µM/L

The impact of endocrine disruptors on the female reproductive system is discussed in a review paper (Nicolopoulou-Stamati and Pitsos 2001). The authors of this review states that there is currently not sufficient data concerning humans and that the limited studies that are there support the hypothesis that endocrine disruptors impair female reproduction.

Currently research conducted on amphibians and birds show a causal relationship between endocrine disruption and EDPs. Preliminary research in humans is showing a relationship between exposure to pesticides and endocrine disruption.

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[3] Pesticides tested were Heptachlor, Aldrin , alpha beta and gamma-Hexachlorocyclohexane, Dichlorodiphenyldichloroethylene (DDE), Dichlorodiphenyldichloroethane (DDD) and Dichlorodiphenyltrichloroethane (DDT)

[4] A wide range of pesticides were reported in this study including, but not limited to, herbicides ( e.g chlorophenoxy), insecticides (e.g organophosphate) and fungicides (e.g organotin).

## 2.7 Fate of Pesticides in Current Water Treatment

Pesticides are continuously introduced into water treatment plants from agricultural run-off (Birkett and Leaster 2002). The fate of pesticides in water is governed by operational parameters, the biodegradability of the pesticides and their physiochemical properties (Barnabé, *et al.* 2009) and water effluent can be a significant source of pesticides.

Water treatment consists of four main stages; preliminary, primary, secondary and tertiary. Preliminary treatment involves the initial screening of the raw effluent to remove large floating objects. Very little removal of organic micropollutants is observed at this stage (Lester and Edge 2001). Pesticide removal in the primary stage is dependent on the pesticides density, size and ability to flocculate as well as the retention time in the tank (sludge retention time) and the surface loading. Many pesticides are hydrophobic and can be adsorbed by fats oils and greases found in effluent waters. The fats oils and greases are then removed typically by a Dissolved Air Flotation process from the surface of the tank and added to the sludge for treatment.

There are a number of removal pathways in secondary treatment including adsorption onto microbial flocs, biological or chemical degradation and transformation and volatilisation during aeration. A study was conducted on the pesticide Lindane and its fate in the conventional activated sludge treatment process was examined (Kipopoulou *et al.* 2004). The study found that sorption on primary sludge solids was the main removal mechanism with removal percentages of 94.3 ± 1.2 %. Lindane losses in the secondary treatment (up to 61 %) suggested biodegradation as the dominant removal mechanism. In a study on conventional drinking water processes it was found that the pesticide Carbazole was detected in solid samples after conventional treatment (Stackelberg *et al.* 2007). In another study, looking at the persistence of compounds in conventional drinking water, the highest concentration of the pesticide Prometron in finished water was found to be 0.096µg/L (Stackelberg *et al.* 2004). Increasing the sludge retention time strongly improves the degradation of pesticide (Birkett and Leaster 2002).

Tertiary treatment is the final clarifying step used. Tertiary treatment can include advanced oxidation processes (AOPs) section (2.8.6), UV treatment (section

2.8.4) and adsorption processes (section 2.8.3) Tertiary treatment is not a requirement under the urban wastewater treatment directive (European Commission. 1991) and therefore tertiary treatment is not that common. Tertiary treatment has been found to be more effective for pesticide removal than secondary treatment.

Another study examined the percentage recovery of pesticides after ten days in chlorinated water (Gibs *et al.* 2007). Results (Table 2-8) show that ten days after treatment pesticides are still present in samples.

**Table 2-8: Percentage recovery of pesticides in water treated with chlorine after 10 days**

| Pesticide | Percentage recovery of compound in preserved sample after ten days |
|---|---|
| Bromacil | 86 |
| Chlorpyrifos | 70 |
| Diazinon | 62 |
| Metalaxyl | 85 |
| Metolachlor | 80 |
| Prometon | 75 |
| Atrazine | 65 |

Pesticides are not removed efficiently from conventional water treatment plants and so other techniques need to be explored.

Most novel techniques now center on a combination of removal techniques to improve removal efficiency. As discussed in sections 2.8.4 and 2.8.5 a large number of removal techniques utilise light to degrade pesticides. Light techniques can be coupled with other techniques such as adsorption and ozonation to improve removal efficiencies.

## 2.8. Studies of Pesticide Removal Techniques

The techniques available to remove pesticides from aqueous solutions are diverse. Pesticides may be physically separated and removed or may be subjected to photo-chemical, chemical and microbial decomposition (Gavrilescu 2005).

Current and novel techniques specifically designed to remove pesticides, in published literature are discussed in this section. Techniques discussed include biodegradation (section 2.8.1), filtration (section 2.8.2), adsorption (section 2.8.3) and photodegradation (section 2.8.4).

### 2.8.1. Biodegradation

Most pesticides are hydrophobic by design so biodegradation is not the primary process for degradation in water treatment (Tomlin 1994). Physical removal such as adsorption to solids is more common. Microbial degradation (biodegradation) is often the main source of pesticide degradation in soils (Waldmann and Shevah 1993). It occurs when fungi, bacteria and other microorganisms in the soil use pesticides as a source of carbon and energy, or consume the pesticides along with other sources of food or energy. Biodegradation rates are dependent upon factors such as soil conditions (temperature, aeration, and pH) and frequency of pesticide application (Gavrilescu 2005).

Pesticides are largely non-polar. This is reflected in the lack of biodegradation studies of pesticides in aqueous solutions as opposed to the wealth of studies conducted on the biodegradation of pesticides in soil environments (Yu, Zhang and Zhou 2011, Zhang *et al.* 2006, Sagar and Singh 2011). Conventional water treatment facilities use the process of biodegradation to achieve break down of pesticides that are present in waters. Most secondary treatment involves aerobic biodegradative processes but anaerobic processes are also utilised (Abusoglu, Demir and Kanoglu 2012). The aerobic biodegradative processes allow the aerobic bacteria contact with oxygen in order to convert organic compounds into water and carbon dioxide. The two most common processes employed are activated sludge and trickling filters. Both of these processes use two vessels: a reactor that contains large populations of microorganisms that reduce the biochemical oxygen demand (B.O.D.) and a clarifier tank where microorganisms are removed from the final effluent. In activated sludge processes most microorganisms are recycled to an aerator at the start of the process whereas in trickling filter processes all of the film containing microorganisms is disposed of (Birkett and Leaster 2002).

There are a number of removal pathways in secondary treatment including adsorption onto microbial flocs, biological degradation and transformation. Numerous chemical factors, such as structural properties and environmental factors, influence biodegradation (Alcock, Sweetman and Jones 1999). Generally, molecules with highly branched hydrocarbon chains are less amenable to biodegradation than un-branched chains and shorter chains are not as quickly degraded as longer chains (Birkett and Leaster 2002).

For triazine pesticides such as Atrazine and Simazine, tests in soil indicate that abiotic (chemical and physical) processes occur during its degradation in wastewater treatment plants. It is suggested that they partition into lipid structures of the biological flocs or chemically bind to bacterial proteins and nucleic acids in the activated sludge. In batch experiments a loss of 25 % for Atrazine and a loss of 33% for Simazine were observed (Leoni *et al.* 1992).

Organochlorine insecticides such as Lindane sorb to the solid phase during the primary and secondary water treatment (Hannah *et al.* 1988). Adsorption is the dominating removal technique for Lindane but biodegradation by co-metabolism does occur (Jacobsen *et al.* 1991).

Chlorophenoxy acid herbicides (such as 2,4-D and MCPA) have a relatively high aqueous solubility and are less lipophilic and more polar than other pesticides and herbicides (Birkett and Leaster 2002). Chlorophenoxy acid herbicides are reasonably biodegradable when spiked into synthetic peptone sewage at concentrations of 5-1000 µg/L and fed continuously into activated sludge reactors (Nyholm *et al.* 1991). 2,4-D was degraded in activated sludge within 7 days (Zipper *et al.* 1999). MCPA was found to have a half-life of one day in a membrane bioreactor (González *et al.* 2006).

### 2.8.2. Filtration

Filtration can be defined as the process of segregation of phases; e.g., the separation of suspended solids from a liquid or gas, usually by forcing a carrier gas or liquid through a porous medium. Filtration differs from adsorption. In filtration it is the physical size of particles that causes separation not the effects of surface charge, as with adsorption. Some adsorption devices containing activated charcoal and ion exchange resin are commercially called filters, although filtration is not their principal function (IUPAC and Calvert JG 1990). Coarse filtration is a common method of primary/secondary water treatment, whether it is sand filtration or purpose built synthetic filters.

Filtration can encompass many techniques that use a membrane for the removal or extraction of unwanted components present in the water. The main types of filtration, that could be used in tertiary water treatment for the removal of pesticides, examined here are: solid phase microextraction (SPME) (Sanchez-Prado *et al.* 2004), nanofiltration (Van der Bruggen *et al.* 2001, Van der Bruggen *et al.* 1998) and reverse osmosis (Bhattacharya *et al.* 2006, Bonné *et al.* 2000).

SPME consists of a short gas chromatography column turned inside out. Fibres coated with an extracting phase, that can be a liquid or a solid are used. SPME is mainly used as a sample preparation method for pesticide residues for example, sample extraction or sample cleanup (Zhang *et al.* 2012).

Nanofiltration can be described as a *pressure-driven membrane-based separation process in which particles and dissolved molecules smaller than about 2 nm are rejected* (IUPAC 1996). Nanofiltration is a membrane filtration process used with surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter. The major advantages of using nanofiltration are its ease of operation, reliability, no additives are required and a modular construction can be utilised to aid in the upscaling of the process (Van der Bruggen *et al.* 2001).

Reverse osmosis can be defined *as a liquid-phase pressure-driven separation process in which applied trans-membrane pressure causes selective movement of solvent against its osmotic pressure difference* (IUPAC 1996). The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. Reverse osmosis is used widely used to remove impurities in drinking water treatment plants.

Forward osmosis can also be utilised in water treatment and is defined as reverse osmosis above but the osmotic pressure itself is the driving force for mass transport not the external pressure that is used in reverse osmosis (Cath, Childress and Elimelech 2006).

Of the types of filtration available to use reverse osmosis is the most commonly studied (Bhattacharya *et al.* 2006, Bonné *et al.* 2000). Even though the contaminants are removed from the water there is still the problem of disposal of the solid waste generated from this technique (Sanchez-Prado *et al.* 2004, Hermosilla *et al.* 2012).

Other filtration techniques such as nanofiltration and solid phase micro extraction (SPME) are not commonly used in large scale operations as they are costly to install and maintain (Liikanen *et al.* 2006). SPME is mainly used for the detection of pesticides in natural water samples (Scheyer *et al.* 2007) as the technique can be used for low concentrations of pesticides. A summary of pesticide removal via filtration is given in Table 2-9.

Glyphosate was removed efficiently (95 %) from simulated wastewater (Liu *et al.* 2012) but this method may not work as effectively in real wastewater due to the presences of natural organic matter (NOM) (Matsui 2002, Matsui 2002).

Atrazine is a commonly studied analyte in filtration studies (Sanchez-Prado *et al*. 2004, Bhattacharya *et al*. 2006, Bonné *et al*. 2000). The highest percentage removal of Atrazine was 99 % and this was found with reverse osmosis (Bonné *et al.* 2000) but another study on the removal of atrazine using reverse osmosis gave 81.7 % removal (Bhattacharya *et al.* 2006). This difference could be due to residence time. Bonné (2000) measured the removal rate over a period of three years where water was continually run through the system whereas Bhattacharya (2006) did not state a time so the residence time could have taken anything from minutes to days.

**Table 2-9: Filtration techniques, parameters and outcomes**

| Removal Technique | Pesticide | Medium | Concentration | Removal %/ Capacity | Reaction time | Reference |
|---|---|---|---|---|---|---|
| Filtration-SPME | Atrazine, Aldrin, Dieldrin, Endrin & Alachlor | deionised water | 200 ng/mL | 95 % | 60 min | (Sanchez-Prado *et al.* 2004) |
| Filtration-SPME | MCPA,<br>2,4-D | rainwater | 0.05 μg/L<br>0.5 μg/L | - | 60 min | (Scheyer *et al.* 2007) |
| Filtration-nanofiltration | Atrazine, Simazine and Diuron | groundwater | 1 μg/L | 90-95 % | - | (Van der Bruggen *et al.* 2001, Van der Bruggen *et al.* 1998) |
| Filtration-nanofiltration | Glyphosate | Simulated wastewater | 500 mg/l | 94.8 % | | (Liu *et al.* 2012) |
| Filtration-reverse osmosis | Atrazine, Simazine and Diuron | deionised water | 0.5 mg/L | 81.7 % atrazine, 75.5 % simazine, 88.7 %diuron | - | (Bhattacharya *et al.* 2006) |
| Filtration- reverse osmosis | Atrazine, Simazine and Diuron | Rhine River water | 20 μg/L | 87 % diuron 99 % atrazine, | no retention decline after 3 yr | (Bonné *et al.* 2000) |

### 2.8.3. Adsorption

Adsorption is an equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility, and simplicity of design, ease of operation, and insensitivity to toxic pollutants (QU 2008). Adsorption also does not result in the formation of harmful substances but there is a disposal issue. The adsorption process is a surface phenomenon that depends on the number of sites available, porosity and specific surface area of adsorbent (Ahmad *et al.* 2010) There are three major categories of adsorbents, carbonaceous, agricultural and other adsorbents (including bioadsorbents and industrial adsorbents).

**Carbonaceous adsorbents**

Carbonaceous materials have been known for a long time to be capable of adsorbing various organic compounds (Ahmad *et al.* 2010). Activated carbon (AC) is one of the most commonly used adsorbents. Amongst its major uses is water treatment processes (SDWC 1980). Activated carbon (AC) is *"a porous carbon material, a char which has been subjected to reaction with gases, sometimes with the addition of chemicals, e.g.* $ZnCl_2$*, before, during or after carbonization in order to increase its adsorptive properties*" (Verhoeven JW 1996). AC is manufactured from various raw materials such as coal, wood, coconut shell, bone, resin but coal is the most common (Ahmad *et al.* 2010). The main steps in the production of activated carbon are carbonization and activation. The carbonization step is usually performed in an inert atmosphere to remove volatile matter. The activation step is an oxidation process with oxidizing gases such as steam, $CO_2$, or air to develop an efficient pore structure. The removal of pesticides from aqueous environments by AC has been reported extensively in the literature (Foo and Hameed 2010b) and forms the main focus of this section. However other adsorbents will also be discussed as comparisons. There are two main types of AC, granular activated carbon (GAC) and powdered activated carbon (PAC)

The adsorptive efficiency of activated carbon is due to its internal pore structure, surface area, and surface reactivity. Activated carbon consists of interwoven micropores, mesopores, and macropores, which are responsible for the high surface area of the carbons and hence high capacity for the adsorption of organic pollutants. The surface functional groups in the activated carbon matrix also play a part in the adsorption of organic molecules (Chingombe, Saha and Wakeman 2006).

In order to evaluate the adsorption capacities of pesticides adsorption isotherms are used. Adsorption isotherms show the amount of adsorbate on the adsorbent as a function of concentration at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials (Sontheimer, Crittenden and Scott Sommers 1988). There are a number of mathematical equations that are used to model the isotherms. The most common are Freundlich and Langmuir. The Freundlich isotherm is empirical i.e. the use of working hypotheses that are testable using observation or experiment. It is used for heterogenous surfaces. For the Langmuir isotherm certain assumptions are made, including that the adsorption occurs in a flat homogeneous surface where two considerations are made. The first consideration is that the solute is chemisorbed on a set of separate localised adsorption sites, all of them releasing the same adsorption energy and the second is that the mobile physical adsorption occurs until only a relatively low coverage is reached (Ruthven M.D. 1984). Isotherm models can be used to determine the maximum sorption capacity and can be used for a better understanding of the binding mechanism (El Bakouri *et al.* 2009).

### Agricultural Adsorbents

Agricultural adsorbents are waste materials and byproducts from agriculture and other industries. They are low cost alternatives to activated carbon due to their abundance in nature. Most of these materials are lignocellulosic (plant biomass that is composed of cellulose, hemicellulose, and lignin). Accumulation of pesticides on agricultural adsorbents is generally achieved through interactions with the hydroxyl and carboxyl groups found in polysaccharides and lignin (Ofomaja 2008). The functionalisation of these materials can result in significant increases in adsorption capacity (Hsu and Pan 2007).

**Other adsorbents**

There are many other types of adsorbents that are utilised for the removal of pesticides including: polymeric, industrial waste, bioadsorbents and inorganic adsorbents. Polymeric adsorbents are polymeric resins that are potential alternatives to activated carbon. Macroporous polymers of nonionic polymeric resins are frequently used in water treatment (Tsyurupa *et al.* 1995, Kyriakopoulos, Doulia and Anagnostopoulos 2005).

Industrial wastes can also be used as adsorbents (Gupta *et al.* 2006). These wastes are low cost materials because of their local availability and cost. Industrial waste adsorbents include wastes such as sludge, fly ash and carbon slurry.

Bioadsorbents are also used to remove pesticides (Alam, Dikshit and Bandyopadhyay 2000). Biosorption has been defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions (Volesky 2007). It is used to indicate a number of metabolism-independent processes such as physical and chemical adsorption, chelation, complexation, ion exchange, electrostatic interaction and microprecipitation. Biosorption takes place in the cell wall rather than oxidation through metabolism. Inorganic adsorbents such as natural clay minerals are also being used to degrade pesticides (Pavlovic *et al.* 2005).

Table 2-10 below shows a summary of all the adsorption studies mentioned in this section.

**Table 2-10: Adsorption removal techniques (all studies listed her used purified laboratory water)**

| Removal Technique | Adsorbent | Pesticide | Concentration | Removal %/ Capacity | Reaction time | Reference |
|---|---|---|---|---|---|---|
| Adsorption-Carbonaceous | GAC: Filtrasorb 400 | Lindane, Alachlor | 10 mg/L | 99 % | 180 min | (Sotelo *et al.* 2002) |
| Adsorption-Carbonaceous | GAC: Filtrasorb 400 + engineered AC | 2,4-D | 10 mg/L | 30 mg/g-35 mg/g (engineered) | 180 min | (Chingombe, Saha and Wakeman 2006) |
| Adsorption-Carbonaceous fibres | AC fibres and GAC | Atrazine | 5 µg/L - 21.4 mg/L | 63-509 mg/g | 48 hr | (Cougnaud, Faur and Cloirec. 2005) |
| Adsorption-agricultural | Chitosan (exoskeleton of crustaceans) | Aldrin, Dieldrin, Heptachlor, Endrin, Endosulfan & Methoxychlor | 2.8 ng/L | Peaks area not detected | 30 min | (Lu, Wang and Sye 2011) |
| Adsorption-agricultural | activated beidellite clay | Alachlor | 2.5 mg/L<br>5 mg/g and 20 mg/g | 5 mg/g<br>16 mg/g (grafted)<br>14 mg/g (acid treated) | 30 min | (Paul, Martens and Frost 2011) |
| Adsorption-agricultural-dates | Acid treated date stones | Aldrin, Dieldrin and Endrin | 0.5 mg/L-10 mg/L | 90 % aldrin and dieldrin<br>78 % endrin | 12 hr | (El Bakouri *et al.* 2009) |
| Adsorption-agricultural-dates | Activated carbon derived from date stones | 2,4-D | 50-400 mg/l | 54 %-92 % | | (Hameed, Salman and Ahmad 2009) |

| Removal Technique | Adsorbent | Pesticide | Concentration | Removal %/ Capacity | Reaction time | Reference |
|---|---|---|---|---|---|---|
| Adsorption-agricultural-bark | Pine bark and AC | Lindane & Heptachlor | 2, 20, 50, 250 and 1000mg dm$^{-3}$ | heptachlor: 93.6 %(bark) 75 % (AC)<br>lindane: 80 %(bark), 98 % (AC) | 24 hr | (Ratola, Botelho and Alves 2003) |
| Adsorption-other-polymer | commercial organic polymer resin<br>Lewatit VP OC 1163 | 2,4-D and MCPA | 20 -400 mg/L | 73 % (2,4-D) 74 % (MCPA) | 20 hr (1.5 min column test) | (Vergili and Barlas 2009) |
| Adsorption-other-industrial waste | Carbon slurry (fertiliser plant )and blast furnace slag, dust and sludge (steel manufacturing plant) | 2,4-D | 6 x10$^{-4}$ M | 212.1 mg/L | 30 min | (Gupta *et al.* 2006) |
| Adsorption-other-industrial waste | Dewatered and liquid alum sludge | Glyphosate | 0.5–500 mg/l | 91.6 % | 52 hr | (Hu, Zhao and Sorohan 2011) |
| Adsorption-other-bio | The macro fungi *sajor caju* and *Florida* were used as adsorbents | 2,4-D & Atrazine | 200 mg/L | 60.3 %(2,4-D),62.3 % (atrazine) | 240 min | (Alam, Dikshit and Bandyopadhyay 2000) |
| Adsorption-other-inorganic | Hydrotalcite $(Mg_6Al_2(CO_3)(OH)_{16} \cdot 4(H_2O)$ | 2,4-D | 1 mM | 59 % | 40 hr | (Pavlovic *et al.* 2005) |

Of the types of adsorbents discussed in this section carbonaceous adsorbents are the most efficient and widely used in water treatment so (Chingombe, Saha and Wakeman 2006, Sotelo *et al.* 2002, Cougnaud, Faur and Cloirec. 2005), therefore these adsorbents will be used as the standards to compare with the other adsorbents. Some examples of the performance of AC compared to other adsorbents are described in the following paragraphs.

For Lindane removal the agricultural adsorbent, pine bark was used (Ratola, Botelho and Alves 2003). When this was compared to activated carbon a difference between percentage removals is noted (99 % with AC and 80 % with pine bark). The authors justify the difference by stating that using pine bark as an alternative to AC would result in savings of up to $17764 per year for Lindane removal at a typical water treatment facility.

For Heptachlor the situation is the opposite where the agricultural adsorbent (pine bark) showed improved percentage removal when compared to AC, 93.6 % (pine bark) and 75 % AC. The fact that one of the pesticides is removed more efficiently than another under the same experimental conditions suggests that pesticides structures play an important role in their removal by adsorbents. Heptachlor is also less soluble in water (0.056 mg/L) than Lindane (8.35 g/l) and would therefore have an affinity to a solid substrate (Tomlin 1994). The adsorption coefficients of Heptachlor and Lindane also differ (24,000 for heptachlor and 11,000 for Lindane). Heptachlor was also used with the agricultural adsorbent, chitosan crab shell (Hu *et al.* 2011). This study stated that Heptachlor was no longer detectable after its treatment with the adsorbent but very low initial concentrations were used (2.0 ng/l and 2.8 ng/l), so this does not support the use of agricultural adsorbents over AC. This group also examined the removal of Aldrin, Dieldrin and Endrin with the same adsorbents giving similar results. When date stones were used as the adsorbent by Bakouri *et al.* (2009) for Aldrin, Dieldrin and Endrin they appear to have worked effectively (8 mg/g of Aldrin was adsorbed from an initial concentration of 10 mg/l). This study used a more feasible pesticide starting concentration of 10 mg/l. Similar results were seen for Dieldrin (7.6 mg/g) and Endrin (6.3 mg/g). The main disadvantage of this study is the use of acid to treat the date stones. Date stones were also used for the removal of 2,4-D

(Hameed, Salman and Ahmad 2009). In this study the date stones were used to derive activated carbon by heating them and acidifying them. Results showed up to 92 % removal efficiency depending on initial concentration.

Overall it can be seen that agricultural adsorbents work effectively at removing pesticides from aqueous environments. Agricultural adsorbents have an initial low cost as they are generally waste products but some sort of pre-treatment is needed for most adsorbents in order for them to be effective. These pre-treatment's range from simple drying (Ratola *et al.* 2003) to complicated chemical grafting (Lu *et al.* 2011). These pre-treatments add to the cost of removal.

Other adsorbents such as polymeric, industrial waste, bioadsorbents and inorganic adsorbents were also investigated as alternatives to AC. Industrial waste adsorbents used for the removal of 2,4-D showed efficient removal (200 mg/g for carbonaceous waste adsorbent and 125 mg/g for Blast furnace sludge (Gupta *et al.* 2006). The results show that the blast furnace waste was a much less efficient adsorbent than the carbonaceous waste, thus showing that carbonaceous adsorbents are the most efficient at removing pesticides. Glyphosate was also efficiently removed (92 %) by using the industrial waste of alum sludge leftover from a water treatment facility (Hu, Zhao and Sorohan 2011) by drying the sludge and performing batch adsorption experiments. The polymer resin Lewatit VP was utilised to remove 75 % of the initial concentration of 2,4-D and MCPA (Vergili and Barlas 2009). The biosorption of Atrazine and 2,4-D was not effective when compared to wood charcoal adsorption (Alam, Dikshit and Bandyopadhyay 2000). For example 60 % removal of 2,4-D was achieved using the biosorbent fungi *sajor caju* but when a wood charcoal adsorbent was used 92.7 % removal of 2,4-D was achieved. Other adsorbents are not as effective as AC and presently do not demonstrate a viable alternative to AC.

Activated carbon, like all adsorbents, has one major drawback and that is its reusability. Once AC has been used fully its pores will become clogged and will need to be washed and treated, which adds to the cost of using activated carbon.

### 2.8.4. Photolysis

Transformations of organic compounds that are a consequence of that compound's own light absorption are called direct photolysis (Schwarzenbach *et al.* 2005). Natural photodegradation utilises sunlight but some chemicals are resistant to direct photodegradation because their absorption spectra differ from the spectrum of sunlight. Indirect photolysis can degrade some of these chemicals using reactive intermediates such as the hydroxyl radical generated from other light absorbing molecules. The light sources used for photolysis can be artificial (UV Lamp) or natural (solar light). Table 2-11 shows studies involving solar photolysis and Table 2-12 shows artificial UV photolysis removal techniques.

**Table 2-11: Solar Photolysis studies**

| Pesticide | Medium | Concentration | Removal %/ Capacity | Reaction time | Reference |
|---|---|---|---|---|---|
| Atrazine | Sea, Lake, distilled and river water | 9 mg/l | 9 mg/l to 2.5 mg/l in distilled (70 %)<br>9 mg/l to 3.5 mg/l in (60 %) | 65 days in distilled<br>65 days in sea and lake water<br>T1/2= 34.5days in distilled | (Konstantinou, Zarkadis and Albanis 2001) |
| Atrazine | Milli-Q water | 2–20 mg $L^{-1}$ | 90-50 µM/L (55 %) (UV)<br>90 µM/L to 55 µM/L (38 %) (solar) | 60 min (UV)<br>45days (solar) | (Prosen and Zupančič-K.L. 2005) |
| MCPA | Thames river water | $2.49 \times 10^{-5}$ M | 90 % | 20 days | (Stangroom, Macleod and Lester 1998) |

**Table 2-12 Summary of UV photolysis removal techniques**

| Pesticide | Medium | Concentration | Removal %/ Capacity | Reaction time | Reference | Light Source |
|---|---|---|---|---|---|---|
| Carbendazim | bi-distilled water | 25-30µM/l | 88 % | 100min | (Panadés, Ibarz and Esplugas 2000) | high pressure mercury lamp 400W |
| Atrazine | ultra-pure water | 10 mg $L^{-1}$ | 84 % remaining | 60min | (HéquetV., Gonzalez C. and Le Cloirec P. 2001) | Medium pressure mercury lamp doped with thalium iodide |
| Atrazine | Milli-Q water system | 100 µM | 100 % | 90min to intermediate | (Bianchi *et al.* 2006) | 15 W immersion low pressure mercury lamp |
| Atrazine Simazine, Terbutryn and Prometryn | Deionised water | 1 (m/m) % solutions | Complete removal | 1.5hr (Prometryn)<br>10hr (simazine)<br>20hr (atrazine)<br>32 hr (terbutryn) | (KissA., Rapi S. and Csutorás 2007) | low pressure mercury vapour lamp (254nm, 15W) |
| Atrazine | Milli-Q water | 2-25 mg/L | 0 % | 4hr | (Parra *et al.* 2004a) | solar simulator with a cut-off filter at $\lambda$ = 290 nm |
| 2,4-D & MCPA | Ultra -pure water | 50 ppm | 90 % (MCPA)<br>40 % 2,4-D | 40 mins MCPA<br>100mins 2,4-D | (Benitez *et al.* 2004) | 15W low pressure Mercury lamp At 254 nm |
| Glyphosate | Deionised water | 42.275 mg/L | 10.9 % | 3min | (Assalin *et al.* 2010) | 125 W; $\lambda$ > 290 nm |

**Summary of photolysis studies**

Photolysis studies on the degradation of pesticides have been conducted in laboratory environments primarily using UV light. The optimum conditions vary depending on the target pesticide and sometimes between similar studies. Atrazine has been used as the analyte in the majority of the studies discussed above (Héquet, Gonzalez and Le Cloirec 2001, Bianchi *et al.* 2006, Kiss, Rapi and Csutorás 2007, Parra *et al.* 2004a, Prosen and Zupančič- 2005, Konstantinou, Zarkadis and Albanis 2001, Sanches *et al.* 2010). The photolytic degradation (both artificial and natural) of Atrazine is efficient with removal percentages ranging from 55-100 %. The removal times also vary from 60 min (UV) to 20 hr (solar). The half-life of atrazine in one study (Hequez et al 2001) was determined to be less than 5 min but in another study (Konstantinou *et al.* 2001) the half-life was determined to be 34.5 days. The significant difference in half-lives can be attributed to the light source used for the studies. Hequet *et al.* (2001) used a medium pressure mercury lamp whereas Konstantinou *et al.* (2001) used natural sunlight. This demonstrates that the intense UV light improves the degradation of atrazine dramatically. Kiss *et al.* (2007) reported that it took 20 hours to completely degrade Atrazine whereas Bianchi *et al.* (2006) reported a 90 min degradation time. The difference here was in the reporting of results as both studies used similar experimental setups (15W medium pressure lamp). Bianchi *et al.* (2006) stated that after 90 min Atrazine was completely transformed to de-chlorinated and detoxified atrazine products on the other hand Kiss *et al.* (2007) stated that 100 % decomposition was achieved after 20 hr. In other words Bianchi *et al.* (2006) did not achieve 100 % decomposition but did achieve complete transformation to intermediates.

Prosen *et al.* (2005) found that the presence of humic acid hampered the degradation of Atrazine (a 10-fold decrease in rate constant was observed). This was due to Atrazine binding to the humic acid (Martin-Neto, Traghetta and Vaz 2001).

The chlorophenoxy herbicides 2,4-D and MCPA were degraded using monochromatic UV light at 254nm (Benitez *et al.* 2004). The fact that the light was monochromatic helped the efficiency of the photodegradation as there is one intense wavelength of light focused on the pollutant mixture as opposed to a range of wavelengths. Most studies use lamps that emit over a range of UV light frequencies. MCPA photodegraded much more efficiently (90 %) than 2,4-D (40 %). The authors put the difference down to the low molar extinction coefficient of 2,4-D 172.7$M^{-1}$ $cm^{-1}$ which they believe suggests that this herbicide is not a very photolabilable compound and that direct photolysis is not a suitable oxidation process for its removal. Glyphosate was removed via photolysis inefficiently with only 10 % removal after 3 mins (Assalin *et al.* 2010).

Solar irradiance takes a much longer time than UV irradiance to degrade compounds as UV lamp efficiencies are constant and solar energy varies on the time of day and on the time of year. Konstantinou *et al* (2001) found that Atrazine photodegradation was less efficient in natural groundwater ($T_{1/2}$= 26.2 days) than in distilled groundwater ($T_{1/2}$ =34.5 days). This was most likely due to the presence of other natural compounds such as humic acid. MCPA was found to photodegrade but only after 20 days in river samples (Stangroom, Macleod and Lester 1998). This demonstrates while sunlight on its own will be able to degrade pesticides, the process takes too long and so further treatment is required.

The use of UV in commercial wastewater treatment plants has a number of drawbacks. Firstly it is energy intensive and therefore costly to use. It also has the problem that UV light cannot penetrate very deeply into water storage tanks and so a flow through reactor system is needed like the one used in Plataforma Solar de Almería (PSA) in Spain (Figure 2-1) (Malato *et al.* 2002b). Pesticides are designed to be photo-stable when dispersed on crops and so high intensities of UV light are required to break them down.

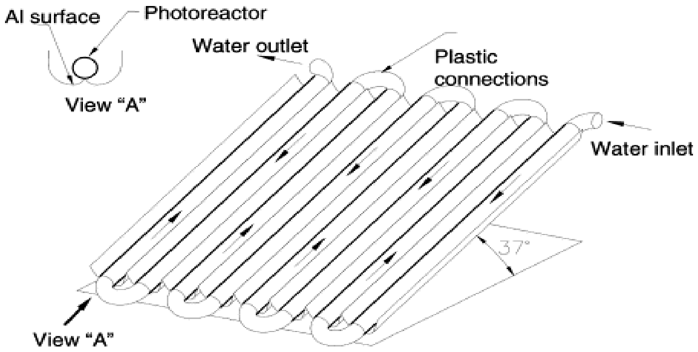


**Figure 2-1 : Solar flow through reactor system used in in Plataforma Solar de Almería**

### 2.8.5. Photodegradation with Photocatalysts

Photolysis is generally too slow and inefficient to be useful in water treatment and so the addition of a photocatalyst is required. Photocatalysis is defined by IUPAC (International Union of Pure and Applied Chemistry) as “Catalytic reaction involving light absorption by a catalyst or by a substrate”. A common photocatalyst is titanium dioxide as it is relatively cheap, non-toxic and chemically stable (Fujino and Matzuda 2006). Photocatalysis experiments can be conducted under UV or solar irradiation. Table 2-13 shows a summary of studies conducted using UV light and photocatalysis for the removal of pesticides.

**Table 2-13: Summary of pesticide removal by UV photocatalysis**

| Pesticide | Medium | Concentration | Removal %/ Capacity | Reaction time | Reference | Catalyst/lamp |
|---|---|---|---|---|---|---|
| 2,4-D | double distilled water | 1m | 96 %<br>95 % TOC | 30 min<br>5 hr | (Trillas, Peral and Domènech 1995) | $TiO_2$ and Pt /$TiO_2$ high pressure mercury lamp |
| 2,4-D | distilled water | 5x $10^{-4}$ M | 100 % mineralisation | 100 min | (Djebbar and Sehili 1998) | $TiO_2$ and ZnO |
| MCPA | distilled water | 5x $10^{-4}$ M | Almost complete disappearance | 100 | (Djebbar, Zertal and Sehili 2006) | $TiO_2$ fluorescent lamp (300-450nm) |
| 2,4-D | agricultural used waters | 20 mg/l | Completely mineralised | Unclear 2000 min | (Herrmann and Guillard 2000) | $TiO_2$/high pressure UV lamp |
| Atrazine | ultra-pure water | 10 mg/l | 94 % | T1/2 20 min | (HéquetV., Gonzalez C. and Le Cloirec P. 2001) | $TiO_{2/}$medium pressure mercury lamp doped with thallium iodide |
| Atrazine | Milli-Q water | 2-25 mg/l | Completely transformed | 45mins | (Parra *et al.* 2004a) | $TiO_2$/xenon lamp |

**Summary of pesticide removal by UV photocatalysis (contd)**

| Pesticide | Medium | Concentration | Removal %/ Capacity | Reaction time | Reference | Catalyst/lamp |
|---|---|---|---|---|---|---|
| Atrazine | Milli-Q water system | 100 µM | 100 % | 4 hrs | (Bianchi *et al.* 2006) | $TiO_2$ /external lamp emitting in the (315–400 nm)& low pressure mercury arc lamp, (253.7 nm) |
| Lindane,<br>Methyl Parathion Dichlorvos | distilled water | 2.5 mg/l (methyl parathion) | 100 % | 25 min (methyl parathion) | (Senthilnathan and Philip 2009) | Suspended and immobilised $TiO_2$ 125W medium pressure mercury lamp (365nm) |
| Glyphosate | Distilled water | 42.275 mg/L | 99.9 % | 30 min | (Assalin *et al.* 2010) | 0.1g of $TiO_2$ /high-pressure mercury lamp (> 290 nm) |

**Solar photocatalysis**

Solar studies using photocatalysis have also been used for the removal of pesticides from aqueous solutions (Parra *et al.* 2004a, Herrmann and Guillard 2000, Senthilnathan and Philip 2009, Muszkat, Bir and Feigelson 1995, Bandala *et al.* 2002, Madani *et al.* 2006). Table 2-14 shows a summary of these studies.

**Table 2-14: Summary of pesticide removal by solar photocatalysis**

| Pesticide | Medium | Concentration | Removal %/ Capacity | Reaction time | Reference |
|---|---|---|---|---|---|
| 2,4-D | agricultural used waters | 10 ppm | TOC reduced from 10 to 2 ppm | - | (Herrmann and Guillard 2000, Herrmann *et al.* 1998) |
| Aldrin | distilled water | 2.5 mg of aldrin in 500 ml of water | 90 % | 120 min | (Bandala *et al.* 2002) |
| Atrazine | distilled water | - | 0 % | 4 hrs | (Parra *et al.* 2004a) |
| Mixed sol of Dichlorvos (d), Methyl parathion (MP) & Lindane (L) | Distilled water | 2.5 mg/l | 100 % | 20 mins (d)<br>160 mins (MP)<br>480 mins (L) | (Senthilnathan and Philip 2009) |
| Diuron | Distilled water | 90 mg/L | 0 % | 120 mins | (Madani *et al.* 2006) |

**Photodegradation with $TiO_2$ on support materials**

Photocatalytic studies can utilise suspensions of the catalysts or materials to support the catalyst. Most reported photocatalytic studies use suspensions of the catalysts. The main advantage of the supported photocatalytic system is that the catalyst can be re-used and there is no need for any post-treatment catalyst filtration step (Parra *et al.* 2004b). An important parameter to consider in the performance of immobilised catalysts is coating thickness (Madani *et al.* 2006).

Most photocatalytic studies use titanium dioxide as the photocatalyst and the most common type studied is P25 (Trillas, Peral and Domènech 1995, Héquet., Gonzalez and Le Cloirec 2001, Bianchi *et al.* 2006, Parra *et al.* 2004a, Djebbar, Zertal and Sehili 2006, Senthilnathan and Philip 2009, Herrmann *et al.* 1998). Other photocatalysts such as zinc oxide have been found to be less effective than $TiO_2$ (Djebbar and Sehili 1998). $TiO_2$ occurs in several phases or polymorphs which are different arrangements of the $TiO_2$ crystal structure. The three polymorphic forms of note are anatase, rutile, and brookite (Figure 2-2) (Foo and Hameed 2010a). The most photoactive form of $TiO_2$ is the anatase phase (Lim *et al*. 2011). P25 is a mixture of anatase and rutile in the region of 70 % – 90 % anatase (Balázs *et al.* 2010).

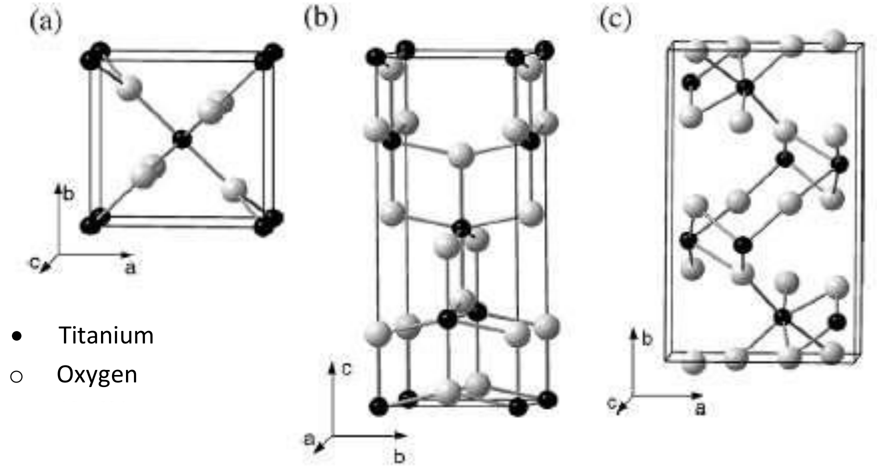


**Figure 2-2: $TiO_2$ polymorphs (a) rutile, (b) anatase, (c) brookite** (Foo and Hameed 2010a)

$TiO_2$ photocatalysis is initiated when light radiation is equal to or higher than the band gap (difference between filled valence band and empty conduction band) of $TiO_2$. Molecular excitation occurs and a redox reaction initiates. Electrons are generated in the conduction band whilst positive holes are generated in the valence band. The positive holes break apart water molecules to form hydron (positive hydrogen cation, $H^+$) and hydroxyl radicals ($OH^-$). This leads to the production of HO◦ radicals. The electrons react with the oxygen molecule to form superoxide anion ($O_2^{-}$◦) and HO◦ radicals. The reaction of HO◦ radicals with the organic pollutant leads to the mineralisation of the pollutant (Teh and Mohamed 2011). The

$TiO_2$ photocatalysis process and reaction steps are summarised in Table 2-15 and a schematic of the reaction is presented in Figure 2.3.

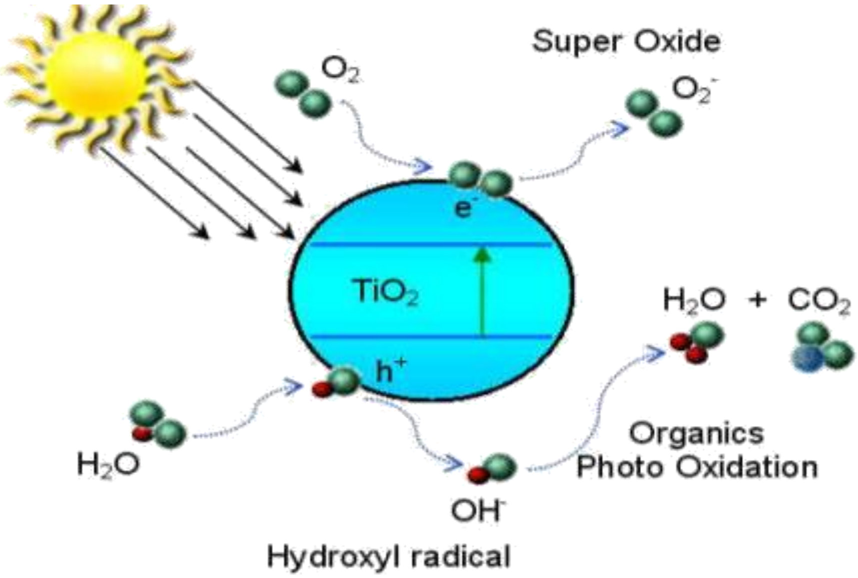


**Figure 2-3 Diagram of $TiO_2$ photocatalysis process showing the generation of hydroxyl radicals and superoxide radicals**

**Table 2-15: Summary of $TiO_2$ photocatalysis process and reaction steps** (Teh and Mohamed 2011)

| **Process** | **Reaction steps** |
|---|---|
| Photo-excited $TiO_2$ generates electron–hole pairs ($hv \geq E_G$) | $TiO_2 \xrightarrow{hv} e^- + h^+$ |
| Photogenerated holes, $h^+$ migrate to catalyst surface and react with water molecules adsorbed on the catalyst surface $H_2O_{ad}$ | $TiO_2(h^+)+h_2O_{ad} \rightarrow TiO_2 + HO\cdot + h^+$ |
| Photogenerated electrons, $e^-$ migrate to catalyst surface and molecular oxygen acts as an acceptor species in the electron-transfer reaction | $TiO_2(e^-) + O_2 \rightarrow TiO_2 + O\cdot^-_2$ |
| Reactions of superoxide anions, $O_2^-$ | $O\cdot^-_2 + H^+ \rightarrow HO\cdot_2$<br>$O\cdot^-_2 + 3HO\cdot_2 \rightarrow HO\cdot + 3O_2 + H_2O + e^-$<br>$2HO\cdot_2 \rightarrow O_2 + H_2O_2$ |
| Photoconversion of hydrogen peroxide to give more HO• free-radical groups | $H_2O_2 + TiO_2(e^-) \rightarrow TiO_2 + HO^- + HO\cdot$ |
| Oxidization of organic adsorbed pollutants (Sad) by HO• onto the surface of the $TiO_2$ | $HO\cdot_2 + S_{ad} \rightarrow$ Intermediates |
| Overall reaction | Organic Pollutant $\xrightarrow{TiO2/hv}$ Intermediates → $CO_2 + H_2O$ |

2,4-D removal with $TiO_2$ was very efficient with removal ranging from 96 % (Trillas, Peral and Domènech 1995) to complete mineralisation (Djebbar and Sehili 1998, Herrmann and Guillard 2000). The 96 % removal was achieved in 30 min. Djebbar *et al.* (1998) found that complete mineralisation could be achieved with the addition of hydrogen peroxide ($10^{-1}$ M) in 100 min. Herrmann *et al.* (2000) achieved the complete mineralisation of 2,4-D. This study did not use hydrogen peroxide but did use agriculturally used water with a mixture of pesticides (1 mM each) solution. The initial concentration of the Herrmann study was $5x10^{-4}$ M (one order of magnitude in the difference in the Djebbar study). Solar studies using $TiO_2$ for the removal of 2,4-D were also conducted (Herrmann *et al.* 1998). It was reported that after 50 min of exposure to sunlight the concentration was reduced to 0 ppm from 30 ppm. This is half the time it took for 2,4-D to be mineralised by using UV light and $TiO_2$ (Djebbar and Sehili 1998) and hydrogen peroxide was used for the Djebbar study. It cannot be determined if the solar study had complete mineralisation. Herrmann (2000) did not state a reaction time so a comparison cannot be made.

Removal of Atrazine was also efficient with photocatalysis. Again the removal rate varies between studies. Complete transformation was achieved in 45 min (Parra *et al.* 2004b), 94 % was removed after 60 min (Héquet, Gonzalez and Le Cloirec 2001) and almost complete degradation was achieved after 4 hrs (removal at 350 min) (Bianchi *et al.* 2006). When light sources are compared it is noted that Hequet *et al.* (2001) and Parra *et al.* (2004) used a medium pressure mercury lamp whereas Bianchi *et al.* (2006) used a low pressure lamp. This explains the large difference between degradation times (45 min and 4 hrs). The light source used can have a significant effect on the degradation rate. With high pressure lamps the degradation efficiency is improved. This is due to increased light radiation intensity, which generates high energy photons (Kabra, Chaudhary and Sawhney. 2004).

Glyphosate was also removed efficiently (99 %) via $TiO_2$ photocatalysis (Assalin *et al.* 2010)

There is a debate in the literature as to whether the pH of the initial pesticide concentration has an effect on the degradation of the pesticides when $TiO_2$ is used. On the one hand Hequet *et al*. (2001) stated that the pH has a significant but relatively weak influence on the degradation. They stated that there was no interaction between pH and $TiO_2$ at low concentrations of analyte. On the other hand Herrmann *et al.* (2000) stated that slightly increasing pH affected the activity of titania poorly. The pH influence varies with each pesticide. For atrazine removal it was stated that pH 4 (Parra *et al.* 2004b) and pH6 (HéquetV., Gonzalez C. and Le Cloirec P. 2001) gave the most efficient removal. For 2,4-D removal it was stated that the degradation increases with increasing pH (pH 6-12) by Djebbar and that increasing pH affects the activity of $TiO_2$ poorly (Herrmann and Guillard 2000). There is no consensus on whether or not high pH values influence the photodegradation of 2,4-D over $TiO_2$ and further research is required in order to obtain a comprehensive solution.

The majority of studies conducted on the removal of pesticides by photocatalysis use $TiO_2$ in a slurry system (suspensions of $TiO_2$ with analyte) but some studies use solid substrates to support the $TiO_{2.}$ The main disadvantage of the slurry system is that suspensions are not suited for large scale applications as a substantial amount of catalyst is needed. Another disadvantage is that of radiation disruption in which absorption and scattering are increased in a slurry system. The main advantage of the supported photocatalytic system is that the catalyst can be re-used and there is no need for any post-treatment catalyst filtration step. $TiO_2$ supports such as Pyrex (Senthilnathan and Philip 2009), glass (Madani *et al.* 2006) and paper (Parra *et al.* 2004a) have been studied by researchers for the removal of pesticides. It appears that catalytic efficiency of $TiO_2$ remains the same (Parra *et al.* 2004a, Senthilnathan and Philip 2009) or slightly decreases (20 %) (Madani *et al.* 2006) when compared to its efficiency in suspension.

### 2.8.6. Advanced Oxidation Processes

Oxidation is a chemical process that can be defined as *“the net removal of one or more electrons from a molecular entity, an increase in the oxidation number of any atom within any substrate or the gaining of oxygen and/or loss of hydrogen of an organic substrate”* (International Union of Pure and Applied Chemistry and Muller 1994). UV light can be utilised to improve the oxidation process. Advances in chemical water and wastewater treatment have led to the development of methods termed advanced oxidation processes (AOPs). AOPs can be defined as oxidation methods based on the intermediacy of highly reactive species such as hydroxyl radicals in the mechanisms leading to the destruction of the target pollutant (Comninellis *et al.* 2008). Categories of AOPs include heterogeneous and homogeneous photocatalysis based on UV irradiation, addition of $H_2O_2$ and ozonation. Examples of these studies are shown in Table 2-16 and are discussed in the solar photocatalysis section of section 2.8.5.

**UV/$H_2O_2$**

Studies involving addition of hydrogen peroxide to a UV system and other UV oxidation techniques for the removal of pesticides can be seen in Table 2-16. In the presence of hydrogen peroxide and UV light, organic compounds can be removed through direct photolysis and hydroxyl radical oxidation (Beltrán *et al.* 2000)

**UV/ $O_3$**

Ozonation is the most commonly investigated advanced oxidation process as it is widely used in drinking water treatment facilities. Ozonation is a chemical process where ozone ($O_3$) is generated and used to oxidise toxic compounds. This can be achieved via direct oxidation by molecular ozone or by indirect oxidation by OH radicals that are formed by the decomposition of ozone in alkaline conditions size (Gültekin and Ince, 2007).

Molecular ozone is generated by Eqn 1 and 2 below:

Eqn (1): $O_2$ + photon (radiation < 240 nm) $\rightarrow$ 2 O◦

Eqn (2): O◦ + $O_2$ + M $\rightarrow$ $O_3$ + M

( M indicates conservation of energy and momentum)

It is destroyed by the reaction with atomic oxygen:

Eqn (3): $O_3$ + O◦ $\rightarrow$ 2 $O_2$

Eqn 3 is catalysed by the presence of certain free radicals, mainly hydroxyl (OH). Ozonation degrades the organic compounds in water to low molecular weights substances. The by-products created by the process can also be harmful to human health (Ikehata and El-Din 2006).

### UV/ Ultrasound

Ultrasound has been extensively used as an advanced oxidation process (AOP) for waste water treatment (Bianchi *et al.* 2006, Petrier, David and Laguian 1996). This is owing to the production of $OH^{\bullet}$ radicals in aqueous solutions and subsequent oxidation of pollutants in the presence of ultrasound (Mahamuni and Adewuyi 2010). Ultrasound can be considered as a microreactor acting as a source releasing H, OH and OOH radicals in water (Petrier, David and Laguian 1996).

**Table 2-16: Summary of pesticide removal by UV oxidation (all studies shown here used laboratory quality water)**

| Removal Technique | Pesticide | Conc. | Removal %/ Capacity | Reaction time | Reference | Notes |
|---|---|---|---|---|---|---|
| UV oxidation-UV/$H_2O_2$ | Malathion<br>Diazinon | 10 mg/L | Complete degradation | 160 min (diazinon)<br>175 min (malathion) | (Doong and Chang 1997) | A 100 W or 450 W medium pressure mercury lamp |
| UV oxidation-UV/$H_2O_2$ | Atrazine and Simazine | 400 µg/L | 60 % (atrazine) and 70 % (simazine)with | - | (IJpelaar *et al.* 2010) | Medium low pressure UV lamps<br>10 mg $L^{-1}$ of $H_2O_2$ |
| UV oxidation-UV/$H_2O_2$ | Simazine | $2.5x10^{-5}$ M | Complete degradation | 15 min | (Beltrán *et al.* 2000) | 0.1M $H_2O_2$<br>low mercury lamp |
| UV oxidation-UV/$H_2O_2$ | 2,4-D and MCPA | 50 ppm | 90 % (MCPA)<br>90 % 2,4-D | 12 min (MCPA)<br>30 min (2,4-D) | (Benitez *et al.* 2004, Assalin *et al.* 2010) | low pressure mercury vapour lamp (254nm)<br>2X $10^{-3}$M $H_2O_2$ |
| UV oxidation-$O_3$ | Atrazine | 90 µM | 80 % transformation into a de-alkylated intermediate | 45 min | (Bianchi *et al.* 2006) | 250 W iron halogenide lamp |
| UV oxidation-$O_3$ | Alachlor | 100 mg/l | -95 % atrazine removal<br>- 55% (catalysed | 30 min (atrazine)<br>180 min (TOC) | (Qu *et al.* 2004) | also used Cu/$Al_2O_3$ catalysed ozonation |
| UV oxidation-O3 | Glyphosate | 42.275 mg/L | 80 % | 30 mins | (Assalin *et al.* 2010) | 14 mg/l (ozone concentration)<br>high-pressure mercury lamp (125 W; λ > 290 nm) |
| UV oxidation-Ultrasound | Pentachlorophenol (PCP) and Atrazine | 0.1 mM | 100 % atrazine & PCP removal (500kHz) | 75 mins (atrazine) 180 mins (PCP) | (Petrier, David and Laguian 1996) | 20 kHz and 500 kHz |
| UV oxidation-Ultrasound & $O_3$ | Atrazine | 90 µM | 100 % | 1 hr | (Bianchi *et al.* 2006) | low pressure mercury arc lamp (253.7nm) |

**Fenton’s Reagents**

Fenton’s reagents consist of peroxides (usually $H_2O_2$) and iron. The peroxides and iron ions form active oxygen species (hydroxyl radicals) that oxidise organic or inorganic compounds. The term “Fenton's reagent” refers to the mixture of hydrogen peroxide and iron ions. The active sites in the Fenton process are derived from iron ions which serve as a catalyst to break down the hydrogen peroxide molecules into numerous hydroxyl radicals (Soon and Hameed 2011).

The degradation rate of organic pollutants is strongly accelerated with photo-Fenton by irradiation with UV–Vis light. Under these conditions, the photolysis of $Fe^{3+}$ complexes allows for rapid $Fe^{2+}$ regeneration and the occurrence of Fenton reactions due to the presence of $H_2O_2$ (Malato *et al*. 2002a).

Fenton or photo-Fenton processes have been found to be an efficient method of removing pesticides from aqueous environments. Some studies even state that the photo Fenton process is more efficient than $TiO_2$ photocatalysis; for example 90 % TOC removal of methomyl can be achieved in 187 min by photo-Fenton or 421 min by $TiO_2$ photocatalysis (Malato *et al.* 2002a). Complete degradation of 2,4-D can be achieved by using photo-Fenton (Pignatello, Oliveros and MacKay 2006, Pignatello 1992).

The main disadvantage to using Fenton’s reagents is the cost of the chemicals involved and if it is to be used as a large scale water treatment process, the costs would be uneconomical. If a Fenton-like process achieved by on-site electrochemical generation of $H_2O_2$ is utilised, an economic savings of as much as 64.5 % in running costs can be achieved (Agladze *et al*. 2007).

### Advanced oxidation processes overall discussion

The addition of $H_2O_2$ increases the degradation rate of the pesticides. Malathion and Diazinon were most efficiently degraded when a combination of UV light, $TiO_2$ and $H_2O_2$ were utilized (IJpelaar *et al.* 2010). The complete removal of Malathion using photocatalysis was achieved in 225 min but when $H_2O_2$ was added the complete removal was achieved in 175 min (Doong and Chang 1997). 2,4-D removal rates increased from 40 % to 90 % with the addition of $H_2O_2$ *(*Benitez *et al.* 2004). On the other hand $H_2O_2$ used on its own with UV light is less effective with maximum of 60 % Atrazine degradation being achieved (IJpelaar *et al.* 2010).

Ozonation also appears to be an effective removal technique for pesticides (Bianchi *et al.* 2006). Ozonation under photolytic conditions gave complete degradation of atrazine in 45 min whereas with $TiO_2$ it took almost 4 hrs *(*Bianchi *et al.* 2006). This is due to the extra OH radical attack created by the presence of ozone. Catalysed ozone ($Cu/Al_2O_3$) was shown to improve degradation when ozone on its own was used (Qu *et al.* 2004). Glyphosate removal efficiency was found to be 80 % after 30 mins when ozonation was applied (Assalin *et al.* 2010)

The use of ultrasonification enhances the degradation of pesticide when combined with other processes such as photocatalysis and ozonation. Atrazine degradation decreased from 4hrs when UV and $TiO_2$ were utilized to 1 hr when ultrasonification was used alongside photocatalysis. The same result was noted when ultrasonification was used alongside ozonation (Bianchi *et al.* 2006). Ultrasonification on its own is also effective in reducing atrazine from 0.1mM to 0mM in 180 min (Petrier, David and Laguian 1996).

Overall these oxidation methods are effective but are even more effective when combined with other processes. However ozone needs high pressures and large energy consumption. The cost of large quantities of hydrogen peroxide needed for large scale pesticide treatment would be prohibitive.

## 2.9 Combination of Adsorption and Photocatalysis

There has been considerable research in the area of combining the adsorption properties of activated carbon with $TiO_2$ photocatalysis (Lim *et al*. 2011). $TiO_2$ powder is nano-sized and it is difficult to recover by conventional solid/liquid separation processes such as filtration or centrifugation and so its use directly in water, is restricted. To address this limitation activated carbon in various forms has been used as a carrier to both immobilize $TiO_2$ and to pre-concentrate the target species (Basha *et al*. 2011).

AC/$TiO_2$ composites are sometimes referred to as Integrated Photocatalytic Adsorbents (IPCAs) (Keane *et al*. 2011). IPCAs consist of either activated carbon coated with $TiO_2$ or $TiO_2$ coated with a carbonaceous material that was heat treated to form an activated carbon. AC emerges as the most attractive $TiO_2$ support for the following reasons:

- AC has the ability to adsorb a wide range of pollutants as well as natural organic matter (NOM) (Delgado *et al*. 2012)
- AC is readily available in different particle sizes
- AC has a long tradition of use in water treatment (Lim *et al*. 2011)
- AC in contact with $TiO_2$ is capable of prolonging the separation lifetime of photogenerated e-/h+ and therefore increasing the rate of $^{\cdot}OH$ radical generation by the photocatalyst (Cordero *et al.* 2007)

Other support/adsorbent materials that have been used with $TiO_2$ include mordenite (zeolite), silica ($SiO_2$) and alumina ($Al_2O_3$) (Ding *et al*. 2001, Yoneyama and Torimoto 2000).

As AC/$TiO_2$ composites are the most documented (Lim *et al*. 2011, Cao *et al*. 2011, Jamil *et al*. 2012, Yap *et al*. 2012, Yap, Lim and Srinivasan 2011) this review in this thesis will be restricted to this type of adsorption/photocatalysis composite. A number of different types of AC have been used for these composites. The three main types are PAC (Ao *et al*. 2008), GAC (Ding *et al*. 2001)(as mentioned in section 2.9.3) as well as activated carbon fibres (ACF) (Hou *et al*. 2009). The most common type of $TiO_2$ used is P25 (Lim *et al.* 2011).

Figure 2-4 illustrates the removal mechanism (generation of ˙OH radicals) by which the AC/$TiO_2$ composite works.

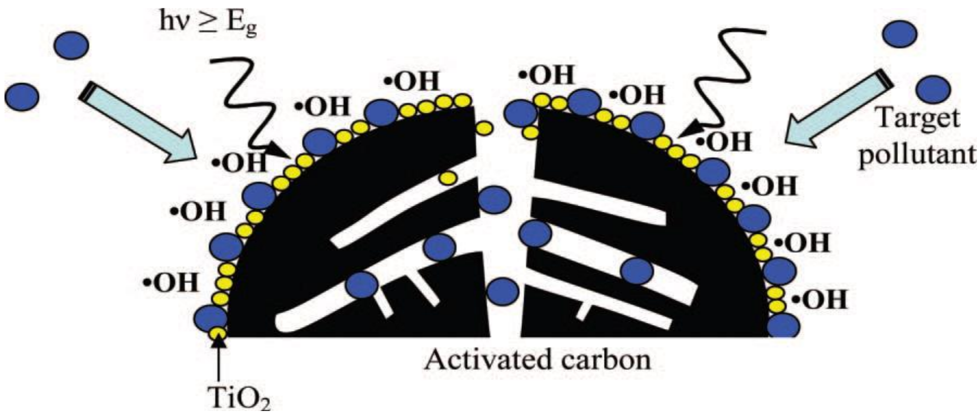


**Figure 2-4 : Schematic illustration of the synergistic effect of adsorption and $TiO_2$ photocatalysis for AC/ $TiO_2$ composite** (Lim *et al*. 2011)

Methods of composite preparation differ between studies but the most common methods are chemical methods such as sol-gel and hydrothermal methods (Lim *et al.* 2011). For the sol-gel methods a titanium precursor such as Titanium-n-butoxide (Ti(Obu)4) is used to coat the AC (Ao *et al*. 2008). Hydrothermal methods generally involve high temperatures for example Liu *et al*. (2007) used a temperature of $500^0$C to prepare the composite (Liu, Chen and Chen 2007).

The ability of these composites to be regenerated and/or reused is a primary consideration if practical applications of the composite are to be demonstrated. Repeated adsorption/degradation tests have been conducted on a limited number of composites using a range of regeneration/degradation cycles. For example one such study (Cao *et al*. 2011, Cao, Oda and Shiraishi 2010) conducted six degradation cycles of their AC/$TiO_2$ composite on the degradation of 2,4 Dinitrophenol , found that removal time increased 1.4 times for the sixth cycle and the adsorption capacity decreased by 18.1 %.

One of the most important parameters to look at in $TiO_2$/AC studies is the pollutant removal performance. A recent review (Lim *et al.* 2011) showed that the most commonly studied pollutants are either organic dyes or simple phenolic compounds, with a limited number of pesticide studies reported in the literature. An example of one such study is Yoneyama *et al.* (2000) where Propyzamide (a pesticide) was a used as the target pollutant. It was determined that 91.5 % of the initial concentration of Propyzamide was removed from aqueous solution after 300 mins when the $TiO_2$/AC composite was used compared to only 1.4 % removal when bare $TiO_2$ was used. It was initially suggested that the use of adsorbent supports retarded the apparent rate of photodecomposition of propyzamide as the rate of decrease of propyzamide was the highest at the bare $TiO_2$. However, the $CO_2$ evolution did not appreciably occur at the bare $TiO_2$ even when propyzamide mostly disappeared. In contrast, $CO_2$ evolution commenced to occur from the beginning of irradiation if the adsorbents were used as the support. A summary of some selected studies and outcomes can be seen in table Table 2-17.

**Table 2-17: AC/$TiO_2$ composite studies and findings**

| Analyte | Removal %/Capacity | Reaction time | Light sources and other parameters | References |
|---|---|---|---|---|
| Propyzamide (pesticide) | 91.5 % | 300 min | 70 wt.% $TiO_2$-loaded adsorbents 500 W xenon lamp | (Yoneyama and Torimoto 2000) |
| phenol | 99.5 % | 100 min | 8 W UV lamp with emission at 365 nm | (Liu, Chen and Chen 2007) |
| Acid Orange II (dye) | 77 % | 180 mins | 15-w germicidal lamp (90 % energy output at 253.7 nm) | (Hou *et al.* 2009) |
| phenol | 5 % | 60 mins | Possibility of pre-adsorbed phenol being released into solution | (Ding *et al.* 2001) |
| Methyl Orange (dye) | 94.2 % (visible)<br>98.6 % (solar) | 180 min | 90 W indoor halogen lamps and natural solar light after 8 runs reduced from 100 % removal to 85 % | (Jamil *et al.* 2012) |
| phenol | 90 % | 6 hrs | Separate addition. no composite 20 W lamp (365 nm) | (Ao *et al.* 2008) |
| Sulfamethazine (antibacterial) | 90 % | 4 hrs | solar simulator equipped with a 150 W Xe arc lamp | (Yap *et al.* 2012) |
| 2,4-dinitrophenol | 99 % (mainly adsorption | 200 min | 6-W blacklight blue fluorescent lamp with a wavelength distribution of 300–400 nm | (Cao, Oda and Shiraishi 2010) |

## 2.10 Concluding Remarks

This review has discussed techniques used in conventional water treatment and focussed on techniques being developed for specialised removal of pesticides. Of the removal techniques discussed here, some techniques may prove to be difficult to standardise such as solar photocatalysis due to varying sunlight levels throughout the day and from country to country. Many of the techniques discussed here were successful in controlled laboratory based studies but did not use real water systems and have not been scaled up. Certain techniques are not fully effective unless used in combination with other techniques, e.g. advanced oxidative processes where a combination of UV light with ozonation and sonication can be employed. Considerable research will be required to establish optimum parameters for each variable of these combination techniques.

Each removal technique has its positive and negative aspects. In addition to the effectiveness of removal techniques, further research will be required to determine those that are commercially viable for removal of pesticides. For example, UV oxidation techniques such as hydrogen peroxide, ozone and ultrasonication can be used in conjunction with photocatalysis to give effective removal techniques; however, the cost of the chemicals would be high for large scale treatment plants and the energy consumption would be large in order to create ozone and maintain ultrasonication.

Each year researchers develop and register new chemicals and new formulations of existing chemicals for pesticide use. This is a constantly evolving area which will necessitate continuous research into cost effective techniques for the removal of pesticides from water systems.

As has been illustrated in this review, there has been a considerable amount of research conducted on both adsorption and photocatalysis as separate removal techniques of pesticides from water. However, very little research has been conducted to date on combining these processes. Therefore, the aim of this project is to develop a series of adsorbent and photocatalyst ($TiO_2$) composites to create an efficient technique for the removal of pesticides from water. The composites will then be fully characterised and tested on two sample pesticides, their removal efficiencies calculated and compared to each other and to existing techniques i.e.

adsorbent or photocatalyst only. The target analytes chosen to investigate these methods were the pesticides 2,4-D and MCPA. These specific pesticides were chosen as they are among the top five commonly applied pesticides in Ireland and Europe, they have been detected in Irish drinking water supplies above their EU limits and methods of detection has previously been developed and validated by this research group. Both pesticides are aromatic compounds with a similar chemical structure however, 2,4-D was expected to be more resistant to photodegradation, due to the presence of two chlorine substituents while MCPA has only one chlorine substituent. It was planned to make a comparison in terms of removal efficiencies.

# 3 Materials and Methods

## 3.1 Materials

### 3.1.1 Composite Materials

P25 (AEROXIDE® P25 $TiO_2$) manufactured by Evonik Industries was donated by the National Chemical Company of Ireland and its properties are shown in Table 3-1. AC Aquasorb 2000 manufactured by Jacobi Carbons was donated by ENVA Water Treatment, Cork, Ireland. The properties of the activated carbon used for AC/$TiO_2$ preparation are detailed in Table 3-2.

**Table 3-1: P25 Titanium Dioxide specifications provided by manufacturer**

| Properties | P25 $TiO_2$ |
|---|---|
| Specific surface area (BET $m^2/g$) | 50±15 |
| particle size (mm) | 0.425-1.70 |
| Behaviour toward water | Hydrophilic |
| Tapped density(g/l) | 130 |
| $TiO_2$ (wt. %) | ≥ 99.5 |
| $Al_2O_3$ (wt. %) | ≥ 0.300 |
| $Fe_2O_3$ (wt. %) | ≥ 0.010 |
| $SiO_2$ (wt. %) | ≥ 0.200 |
| pH (usage range) | 3.5-4.5 |
| Main Purpose | Pigmentation |
| Other Purposes | Photocatalyst |

**Table 3-2: Activated carbon specifications provided by manufacturer (Jacobi)**

| Properties | Aquasorb 2000 |
|---|---|
| surface area ($m^2/g$) | 1050 |
| particle size (mm) | 0.425-1.70 |
| iodine number (mg/g) | >1000 |
| pore volume ($cm^3/g$) | 1.04 |
| ash content (%) | <15 % |
| moisture content (wt. %) | <5 |
| AC type | GAC |
| pH (usage range) | 8-11 |
| Purpose (for context of this project) | Water treatment |
| Methylene Blue number | 280mg/g |

The Porphyrin dyes 5,10,15,20-Tetrakis-(4-carboxyphenyl)-21,23H-porphyrin (97 % dye content) and 10,15,20-Tetrakis-(4-bromophenyl)-21,23H-porphyrin were purchased from Porphyrin Systems, Germany. Methylene Blue (98 % dye content) was purchased from Sigma Aldrich, United Kingdom.

### 3.1.2 Target Analyte Materials

The pesticides 2,4-Dichlorophenoxyacetic acid (2,4-D) and 4-Chloro-2-methylphenoxyacetic acid (MCPA) were purchased from Fluka, Buchs, Switzerland (97 % purity). The comparator analyte Famotidine was donated by Astellas Ireland.

### 3.1.3 Other Materials

Hydrogen peroxide (35 %) was purchased from Sigma Aldrich, Ireland. HPLC grade methanol and water were purchased from Fisher Scientific Ltd., Dublin, Ireland. Formic acid (>98 %) was purchased from Fluka, Buchs, Switzerland. Amber HPLC vials were purchased from VWR International, Dublin, Ireland. Glass fibre filter paper (FB59077) with a diameter of 90 mm, equivalent to Whatman No. 3 were purchased from Fisher Scientific, Ireland while 0.22 µm nylon syringe filters were purchased from Phenomenex Inc., United Kingdom. Pall nylon filters (0.2 µm pore size 47 mm diameter) were purchased from Sigma Aldrich. A Bransonic® ultrasonic cleaner (5510 E-Mt) was used for mobile phase degassing and Ac/$TiO_2$ composite preparation. Dolomite both in its powdered and granular form was donated by The Questor Centre, Belfast, Northern Ireland.

## 3.2 Methods

### 3.2.1 Synthesis of composites

The synthesis of these composites is integral to each experimental run and so the synthesis of AC/$TiO_2$ composite is described in detail in chapter 4 and the synthesis of composites two (dye/$TiO_2$) and three (Dolomite/$TiO_2$) are described in detail in chapter 5.

### 3.2.2 Sorption experiments for AC/$TiO_2$ composite

Batch equilibrium sorption experiments were performed by agitating 0.05 g of AC or 0.05 g of the composite in 100 ml of 2,4-D and MCPA solutions of various initial concentrations ranging from 0.05 to 0.6 mmol/L with their unadjusted pH values (3.39 for 2,4-D and 3.43 for MCPA). Batch adsorption experiments were also conducted on Famotidine for comparison purposes. The solutions were shaken using a G10 Gyrotory shaker, New Brunswick Scientific, Eddison, USA at 100 rpm for 48 hrs in the dark. Samples of 1 ml were taken at regular intervals (beginning with every 20 mins for the first two hours then gradually increasing to every four hours) over the 48 hr period until equilibrium was established. The pesticide solutions were prepared using a 10 mmol/L stock solution of each pesticide by dissolving 0.2006 g (MCPA) and 0.2210 g (2,4-D) in 100 ml of methanol.

Isotherms are adsorption equilibrium studies that are defined at a constant temperature (Sontheimer, Crittenden and Scott Sommers 1988). In the current study it was found that 48 hrs was sufficient for equilibrium to be reached for both 2,4-D and MCPA onto both AC and composite. After equilibration the samples were syringe filtered with Phenomenex 0.22 µm nylon filters, UK to remove any composite, $TiO_2$ or AC particles in the sample and then analysed using high performance liquid chromatography (HPLC). The pH was recorded before and after adsorption. All experiments were conducted in triplicate and included adsorbent-free controls at each concentration.

The results of the isotherm tests are plotted as the equilibrium solid phase concentration (q) versus equilibrium liquid phase concentration (c). q is determined by the following equation:

$$q=(c_0-c)*V/M \qquad (2.1)$$

Where V= volume of the adsorbate solution (L), $c_0$ = the initial/control liquid phase concentration of the analyte, c = the equilibrium liquid phase of concentration of the analyte and M =mass of adsorbent. c is determined from the method of detection.

### 3.2.3 Photodegradation experiments

*AC/TiO₂ composite photodegradation*

Photodegradation experiments were conducted in borosilicate glass photochemical reactors. A 200 ml capacity photoreactor was used for initial studies as well as an immersion well 300 mm in length with water cooling. A 125 W medium pressure mercury lamp (TQ 150 Heraeus Noblelight, emission between 248 and 579 nm, $\lambda_{max}$ 366 nm) inserted in the middle of the reactor was used as the light source for AC/$TiO_2$ experiments. The reactor and light source were placed in an aluminium lined cupboard. The AC/$TiO_2$ composite and pesticide solution in the photoreactor were mixed using a magnetic stirrer (shown below in Figure 3-1 and Figure 3-2)

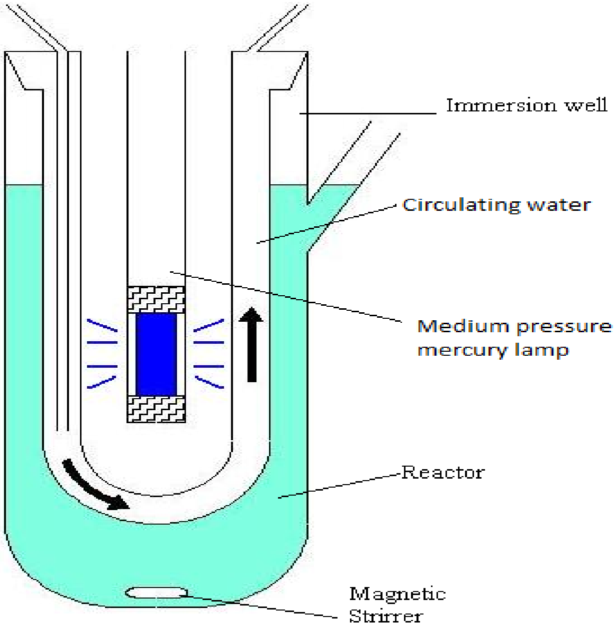


**Figure 3-1: Schematic of photodegradation for AC/$TiO_2$ composite**

**Figure 3-2: photograph of photodegradation of AC/$TiO_2$ composite**

**Photodegradation system for AC/$TiO_2$ composite**

Direct photolysis studies were undertaken using UV irradiation in the absence of catalyst to determine the baseline pesticide photodegradation rate. For photodegradation studies a catalyst concentration of 0.3 g of AC/$TiO_2$ composite per 200 ml was used. The analyte solution and composite suspension were stirred in the dark for 90 min, before illumination, to allow adsorption to stabilise. The change of the analyte concentration during UV irradiation was measured by withdrawing 3 mL samples of the solution from the reactor at defined intervals (Table 3-3). These samples were syringe filtered with 0.22 $\mu$m nylon filters from Phenomenex, UK to remove any composite particles in the sample and then refrigerated in the dark in 10 ml plastic tubes before analysis (section 3.3.3).

**Table 3-3: Sampling regime (AC/$TiO_2$ composite)**

| Sample Type | Sample Time (min) |
|---|---|
| Control (pesticide solution only) | prior to addition of composite |
| Test sample (pesticide with composite) | 0 |
| Dark | 15<br>30<br>45<br>60<br>90 |
| UV light | 105<br>120<br>135<br>150<br>180<br>210<br>240<br>270<br>300 |

### ***Dye/TiO$_2$ Composite Photodegradation***

A 500 mL capacity photoreactor manufactured by VWR International, Ireland was used for the photodegradation studies using dye/TiO$_2$ composites. Initial experiments were performed using a 100 ml capacity reactor. It was decided to increase the capacity of the reactor to enable improved stirring of the composite, to increase sample volumes and to improve light penetration. The light source used was a 500W halogen lamp emitting light in the visible region (390 nm-700 nm) as the dyes absorb light in the visible region. The lamp was placed outside the reactor as it was too large to fit internally. This meant that light was directed at one half of the reactor while the other half of the reactor absorbed only reflected light. The composite and target pesticides solution were stirred using a magnetic stirrer. A schematic of the experimental apparatus is shown in Figure 3-3. The weight of dye/TiO$_2$ composite used in the photodegradation experiments was 0.155 g for porphyrin experiments and 0.145 g for methylene blue experiments as used in an earlier study (Murphy 2012). Adsorption in the dark was not examined as TiO$_2$ on its own does not adsorb the analytes efficiently (<50 %) and the powder dye does not provide a large surface area for adsorption to occur. This was demonstrated experimentally in TiO$_2$ adsorption studies (discussed in section 4.4). After 48 hrs only 27 % of the initial 0.5 mmol/L of MCPA was adsorbed. These photodegradation studies only lasted 3 hrs. The sampling regime was slightly altered for the dye/composite photodegradation experiment (Table 3-4) as there was no adsorption time and in order to compare results to previous studies (Murphy 2012).

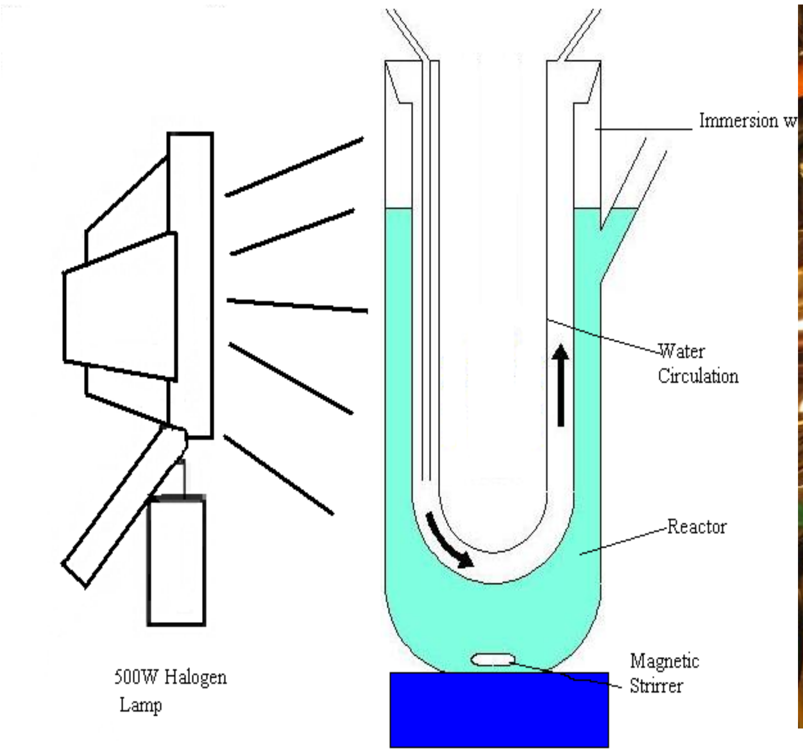


**Figure 3-3: Schematic of photodegradation for dye/TiO$_2$ composite**

**Figure 3-4: Photograph of photodegradation of dye/TiO$_2$ composite**

**Table 3-4: Sampling regime (dye/TiO$_2$ composite)**

| Sample Type | Sample Time (min) |
|---|---|
| Control (pesticide solution only) | prior to addition of composite |
| Test sample (pesticide with composite) | 0 |
| Visible light (halogen light) | 20 |
| | 30 |
| | 40 |
| | 50 |
| | 60 |
| | 80 |
| | 100 |
| | 120 |
| | 140 |
| | 160 |
| | 180 |
| | 270 |
| | 300 |

***Dolomite/$TiO_2$ composite photodegradation studies***

The photodegradation experiments using Dolomite/$TiO_2$ were carried out in the same manner as that of the AC/$TiO_2$ composite. 0.3 g of the dolomite composite was used in all the studies. The equipment used was as in Figure 3-1 and the sampling regime as in Table 3-3.

### 3.2.4 Hydrogen Peroxide/$TiO_2$ experiments

Hydrogen peroxide ($H_2O_2$) experiments were conducted in the 200 ml borosilicate glass photoreactor as outlined in section 3.2.3, which is the same as for AC/$TiO_2$ composite photodegradation studies. The concentration of $H_2O_2$ used in the photoreactor was 100 mg/l. Control experiments were conducted with the target analyte in the presence of $H_2O_2$ in deionised water. Experiments were also conducted with 0.3 g of $TiO_2$ in the presence of 100 mg/l of $H_2O_2$. Samples were taken every 20 mins once the light was switched on. The light source used was the 125 W medium pressure mercury lamp (TQ 150) as that used in the photodegradation of the AC/$TiO_2$ composite.

## 3.3 Analysis

Characterisation of each composite was conducted to visualise the physical structure and to analyse the elemental components of the composites. This was done by using a combination of microscopy and spectroscopy. A brief description of the techniques used to characterise the composite is given below. More details on the techniques are provided in chapters 4 and 5.

In order to analyse the removal efficiencies of the composites and the extent of photodegradation it was necessary to utilise methods for the detection and quantitation of target analytes remaining in solution. UV-Vis spectrophotoscopy, High Performance Liquid Chromatography and Mass Spectrometry were utilised for this purpose.

### 3.3.1 Characterisation of the composites

FEI's high resolution Scanning Electron Microscope (SEM), Quanta 650 FEG, equipped with Oxford Instrument EDS, X-MAX20 SDD detector from the Tyndall Institute was used to characterise the AC/$TiO_2$ composite. SEM is used to analyse the microstructure morphology and chemical composition of the composite. This is achieved by enlarging the visual angle through the optical lens by using high energy electron beams to deflect electrons in a magnetic field (Zhou and Wang 2007). Samples are sputtered in gold prior to analysis in order to ionise the surface area for imaging.

Energy-dispersive X-ray spectroscopy (EDX) was also performed on the AC/$TiO_2$ composite. The technique is used for the elemental analysis of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample (Zhou and Wang 2007).

A Jasco V-670 UV/Vis/NIR spectrophotometer (Essex, UK) with a diffuse reflectance integrating sphere was used to characterise the porphyrin/$TiO_2$ composite. Diffuse Reflectance Spectroscopy is useful for this composite as it has the consistency of a finely ground powder and this technique can be used to obtain molecular spectroscopic information. Reflection of incident radiation from powder will be diffusely scattered in all directions. The spectrum is obtained by the collection and analysis of surface-reflected electromagnetic radiation as a function of wavelength (Mirabella 1998).

X-Ray Diffraction (XRD) was performed on the dolomite/$TiO_2$ composite using a Bruker D8 Advance GX002 X-ray diffractometer with a NaI scintillator detector. This method is mainly used to characterise crystalline structures. An X-ray beam incident on a material penetrates micrometers into the bulk and the direction of the diffracted beam intensity is determined by the periodicity of the atom planes in the material (Flewitt and Wild 1994).

### 3.3.2 UV-Vis Spectroscopy

Initially, photodegradation experiments using the procedures outlined above were analysed using a Beckman DU 520 general purpose UV-Vis spectrophotometer and a quartz cuvette from Fisher Scientific, Dublin, Ireland. The samples were scanned and peak values at 283 nm and 279 nm for 2,4-D and MCPA respectively were used. When samples that were previously run on UV Vis from earlier experiments were run on the HPLC for comparison it was found that unexpected peaks were evident on the chromatograms at the same target wavelength for both analytes (283 nm and 279 nm for 2,4-D and MCPA respectively.) This meant that when samples were run on the UV-vis larger peaks were seen. These peaks were a mixture of the un-separated degradation peaks and analyte peaks. In order to separate the analyte peak from any other possible intermediate peaks, liquid chromatography was utilised.

### 3.3.3 High Performance Liquid Chromatography

MCPA and 2,4-D concentration were measured using a high performance liquid chromatography (HPLC) system consisting of a Varian 9012 solvent delivery system, Rainin Dynamax AL-200 automatic sample injector and a Varian 9050 variable wavelength UV-vis detector (now Agilent Technologies, Palo Alto, CA, USA). A 150 x 4.6 mm, 3.5µm particle Waters C18 reverse phase column was used for separation of the analyte. 1.5mL short thread amber glass vials, purchased from VWR international, Dublin, Ireland were used. The detection method was based on a previous study (Engels 2012) but modified by using a different instrument and column. The mobile phase consisted of 80 % methanol and 20 % water with 0.1 % formic acid. This solution was filtered by 45 mm, 0.2 µm Pall nylon filters and degassed by ultrasonication for 30 min. The eluent flow rate was 1.0ml/min, injection volume 50 µl and stop time was 7 min. The wavelength of the detector was set at 279 nm (MCPA) and 283 nm (2,4-D). Examples of the resulting chromatograms are shown in Figures 3.5 and 3.6. Data were processed by Varian Star Chromatography Workstation system control software version 6.41.

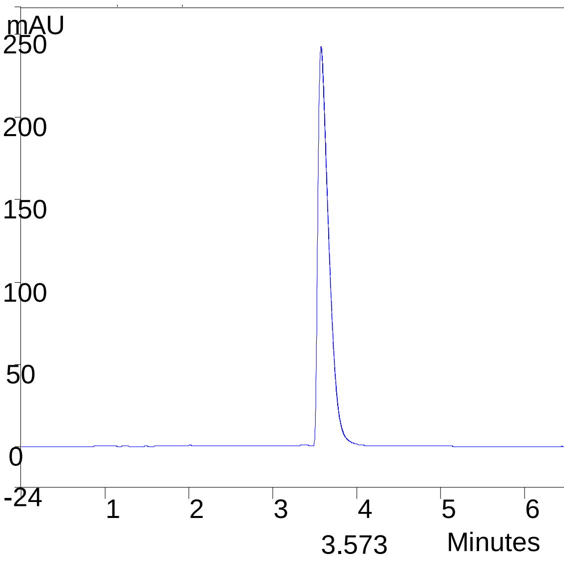


**Figure 3-5: HPLC chromatograph of 2,4-D 0.6mmol/L standard scanned at 283 nm**

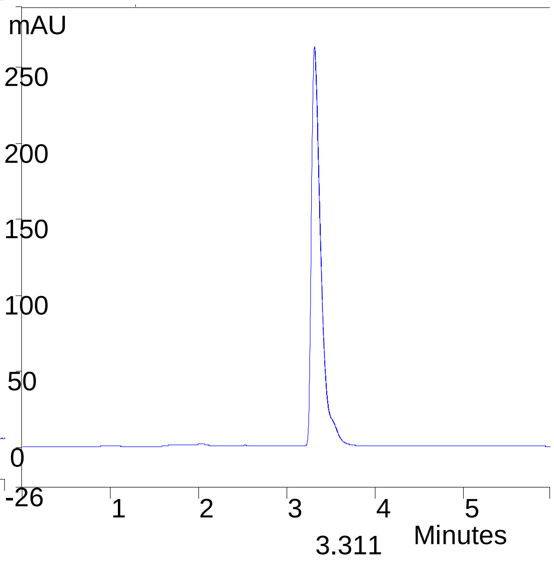


**Figure 3-6: HPLC chromatograph of MCPA 0.6mmol/L standard scanned at 279 nm**

The HPLC method used was validated using the following parameters: precision, accuracy, limit of detection, limit of quantitation, linearity and range, capacity factor, tailing factor and theoretical plates. The method was validated in a previous study by a colleague working with the same analytes (2,4-D and MCPA) (Engels 2012). The HPLC method used for this study was conducted using a different column and a different instrument to those used in the validated method so the ruggedness of the validated method was tested by comparing the limits of detection (LOD), limits of quantification (LOQ) and Relative Standard Deviation (RSD) as shown in table Table 3-5.

**Table 3-5: Validation data for methods 1 (This study) and 2 (Engels 2012)**

| Method | Analyte | LOD (mmol/L) | LOQ (mmol/L) | %RSD of 6 injections of 0.6mmol/L |
|---|---|---|---|---|
| Method 1 | 2,4-D | 0.0027 | 0.0081 | 0.29 |
| Method 2 | | 0.0011 | 0.0035 | 0.08 |
| Method 1 | MCPA | 0.0037 | 0.0111 | 0.54 |
| Method 2 | | 0.0022 | 0.0067 | 0.20 |

The variance in the RSD values shows that the method 2 is slightly more precise than method 1 but still well within the +/- 5 % RSD allowed tolerance. The difference in RSD values is mainly due to the age of the instrument and column. Method two uses more sophisticated instrumentation and software than method one.

### 3.3.4 Mass Spectrometry

The HPLC chromatograms of analyte samples that had undergone photocatalysis with $TiO_2$ and UV light showed intermediate peaks. This demonstrated that further analysis needed to be conducted using mass spectrometry to identify the breakdown products.

A Bruker Daltonics HCT ion trap mass spectrometer equipped with an atmospheric pressure interface-electrospray ionisation (API-ESI) source was used for this purpose. Nitrogen, used as a nebulising and desolvation gas, was provided by a high purity nitrogen generator, available on site through tap, and helium (99.999 %) (BIP-X47S, Air Products, Plc, Crewe, UK) was used as a collision gas. Optimisation of electrospray MS/MS conditions for the dry gas flow, drying temperature, nebuliser pressure, capillary voltage, end plate offset, octopole DC voltage, octopole RF, trapdrive and lenses was carried out by direct infusion using a Cole-Parmer 74900 Series syringe pump set to deliver 300 µL $hr^{-1}$ of analyte solution from a 500 µL glass syringe. The samples were diluted in HPLC mobile phase and the instrument was run in negative mode. Positive ion mode was investigated first but greater sensitivity was achieved in negative ion mode. Negative ion mode was chosen as most literature on these analytes uses negative ion mode (Majzik *et al.* 2006, Santilio, Stefanelli and Dommarco 2009). The system was optimised using 5 ppm standards of both the analytes and results of the optimisation are shown in Table 3-6 and Table 3-7. Samples were directly infused into the mass spectrometer system bypassing the liquid chromatography system.

**Table 3-6: Optimisation parameters for the mass spectrometry system**

| Optimisation Parameter | Value | Range | Value | Range |
|---|---|---|---|---|
| | 2,4-D | | MCPA | |
| Precursor ion (Dα) | 221 | | 199.7 | |
| Capillary (V) | 4266.67 | (1000-5000) | 4200 | (1000 - 5000) |
| Skimmer (V) | -15 | (-100--15) | -27.75 | (-100--15) |
| Cap Exit (V) | -83.3 | (-300--50) | -91.67 | (-300--50) |
| Oct 1 DC (V) | -7.67 | (-20--2.8) | -10.25 | (-20--2.8) |
| Oct 2 DC (V) | -0.43 | (0--2) | -0.2 | (0--2) |
| Trap Drive (V) | 20 | (28-32) | 27.17 | (0-50) |
| Oct RF (V) | 145.83 | (0-300) | 112.5 | (50-300) |
| Lens 1 | 1.25 | (0--15) | 3.25 | (0 -- 15) |
| Lens 2 | 25 | (10-100) | 49 | (10 -100) |

**Table 3-7: Average optimised values for both analytes on the mass spectrometer**

| Average Optimised parameters | |
|---|---|
| Capillary | 4200 |
| Skimmer | -20 |
| Cap Exit | -87 |
| Oct 1 DC | -9 |
| Oct 2 DC | -0.3 |
| Trap Drive | 19 |
| Oct RF | 130 |
| Lens 1 | 2 |
| Lens 2 | 35 |
| Nebuliser | 20 |
| Dry gas | 8 |
| Dry Temperature | 300 |

## 3.3.5. Mathematical Models

Isotherm data must be described by a mathematical model in order to quantify adsorption (Sontheimer, Crittenden and Scott Sommers 1988). There is not a single model that can be used to describe the results of every experiment however most isotherms are described using the Langmuir and Freundlich models. In this study the Redich-Peterson and Toth models was also investigated.

Langmuir equation:

$$\frac{c}{q} = \frac{1}{Qm\,.\,b} + \frac{c}{Qm} \qquad (3.1)$$

Where c = equilibrium liquid phase concentration, q = equilibrium solid phase concentration, $Q_m$ = solid phase concentration when there is a monolayer of analyte adsorbed and b is proportional to the energy of adsorption.

Freundlich equation:

$$q = k^{*}\ c^{\frac{1}{n}} \qquad (3.2)$$

Where c = equilibrium liquid phase concentration, q = equilibrium solid phase concentration, k = Freundlich constant, and 1/n = Freundlich exponent.

Redlich-Peterson equation:

$$q = \frac{k * c}{1 + b * c^{\beta}} \qquad (3.3)$$

Where c = equilibrium liquid phase concentration, q = equilibrium solid phase concentration, k, b and β are regressed Redlich-Peterson constants.

Toth equation:

$$q = \frac{Qm * c}{(1 + \alpha * c^{\beta})^{\frac{1}{\beta}}} \qquad (3.4)$$

Where c = equilibrium liquid phase concentration, q = equilibrium solid phase concentration when β= 1 it yields a Langmuir isotherm and α=0 result in a linear isotherm.

### 3.3.6 Statistical analysis

Statistical analysis was performed on data generated from adsorption studies. The regression coefficient ($R^2$), standard error of estimates (SE), sum of squared error (SSE), average percentage absolute error (% Abs) and root mean squared error (RMSE) were all used to analyse adsorption data.

The regression coefficient indicates how well data points fit a line or curve and can be determined by plotting a relationship (In this case q loading value vs.

time). It provides a measure of how well observed outcomes are replicated by the model. The closer the regression coefficient is to 1 the better the fit of the model to the data.

In order to evaluate the fitness of the equation model to experimental data an error function is required (Kundu and Gupta 2006). The standard error of estimates can be defined as:

$$\mathrm{SE} = \sqrt{\frac{1}{\mathrm{m}-\mathrm{p}}\sum_{\mathrm{i}-1}^{\mathrm{m}}(\mathrm{Qi}-\mathrm{qi})^2} \tag{3.5}$$

The sum of squared error can be defined as:

$$\mathrm{SSE} = \sum_{\mathrm{i}-1}^{\mathrm{m}}(\mathrm{Qi}-\mathrm{qi})^2 \tag{3.6}$$

The Root Mean Squared Error can be defined as:

$$\mathrm{RMSE} = \sum_{i-1}^{m}\frac{(\mathrm{Qi}-\mathrm{qi})^2}{\mathrm{m}} \tag{3.7}$$

Where $q_i$ is the loading observation from the batch experiment I, $Q_i$ is the estimate from the isotherm to for the corresponding qi, m is the number of observations in the experimental isotherm and p is the number of parameters in the regression model. The smaller the SE and SSE values the better the curve fit.

# 4 Results and Discussion for removal of pesticides 2,4-D and MCPA by Activated Carbon/$TiO_2$ Composite

## 4.1. Introduction

This composite is composed of $TiO_2$ coated activated carbons and works in two ways at the same time to remove pollutants; 1) by physical removal via adsorption onto the activated carbon and 2) by photodegradation using photocatalysis with UV light and $TiO_2$. In order to evaluate the removal performance of this composite each process must be looked at separately to collect necessary baseline data. To evaluate the adsorption process sorption studies were conducted and graphed as isotherms (the equilibrium of the sorption of a material at a surface at constant temperature).

The composite was prepared using a low temperature impregnation method as described in section 4.2 . Initially 10 % $TiO_2$ loading composites were prepared as this percentage of $TiO_2$ was previously found to be most effective for the removal of pharmaceuticals (Keane *et al.* 2011, Basha *et al.* 2010). The composite was then optimised to be used in the photodegradation studies. Optimisation parameters included reactor volume, batch reproducibility, weight of composite, composition of composite, pH and initial concentration of pesticide. In each optimisation experiment one parameter was investigated while all other parameters remained constant. For the photodegradation studies the test solution was kept in the dark in order to demonstrate adsorption equilibrium and then the solution was irradiated with UV light (between 248 and 579 nm) to show the effect of photocatalysis. For all the photodegradation studies (except one which investigated the effect of the initial herbicide concentration) an initial concentration of 0.5 mmol/L (equivalent to 100 ppm for MCPA and 110 ppm for 2,4-D) was used. The 0.5 mmol/L initial concentration was chosen as this would have the ability to show degradation over a period of 3-4 hours. If a lower concentration was chosen no significant effect would be visible within the time frame and if it was higher it would be too concentrated to compare it to a realistic concentration found in wastewater.

Once the system was optimised analysis was then performed on both the adsorption and photodegradation components of the system. In order to do this activated carbon and $TiO_2$ controls were examined. It was determined that adsorption was the dominating process and that the composite did not efficiently photodegrade the chosen analytes from solution.

## 4.2. Preparation of AC/$TiO_2$

A low temperature impregnation method using ultrasonication was developed for applying $TiO_2$ to the surface of AC as it was shown to be the most effective and efficient method by Keane *et al.* (2011). Aquasorb 2000 was chosen as the adsorbent substrate as it was previously found to be the most effective activated carbon for this particular use (Keane *et al*. 2011). Aquasorb 2000 was added to the P25 ($TiO_2$) and mixed via ultrasonication. The composite was denoted by its $TiO_2$ loading ranging from 5 to 50 % $TiO_2$ to AC. The percentage mass indicates the proportion of $TiO_2$ that was added to the solution containing the AC before 1 h of sonication in an ultrasonic bath. For example for 3 g of a 10 % composite, 0.3 g of $TiO_2$ was added to 2.7 g of AC. Following overnight oven-drying at 110°C the resulting composites were washed with deionised water to remove any excess P25. Finally the composites were air dried at 110°C and stored in sealed amber glass vials before use.

## 4.3. Characterisation of AC/$TiO_2$ Composite

In order to determine how the $TiO_2$ coated onto the activated carbon scanning electron microscopy (SEM) was utilised. (Details of the SEM and how it works are described in section 3.3.1.) Firstly the AC on its own was imaged. The SEM is capable of imaging the individual grains of AC (approximately 1 mm in diameter) as shown Figure 4-1. With the use of SEM the individual pores of the activated carbon granule can also be determined as shown in Figure 4-1. These images confirm the presence of macro, meso and micropores on the surface of the activated carbon.

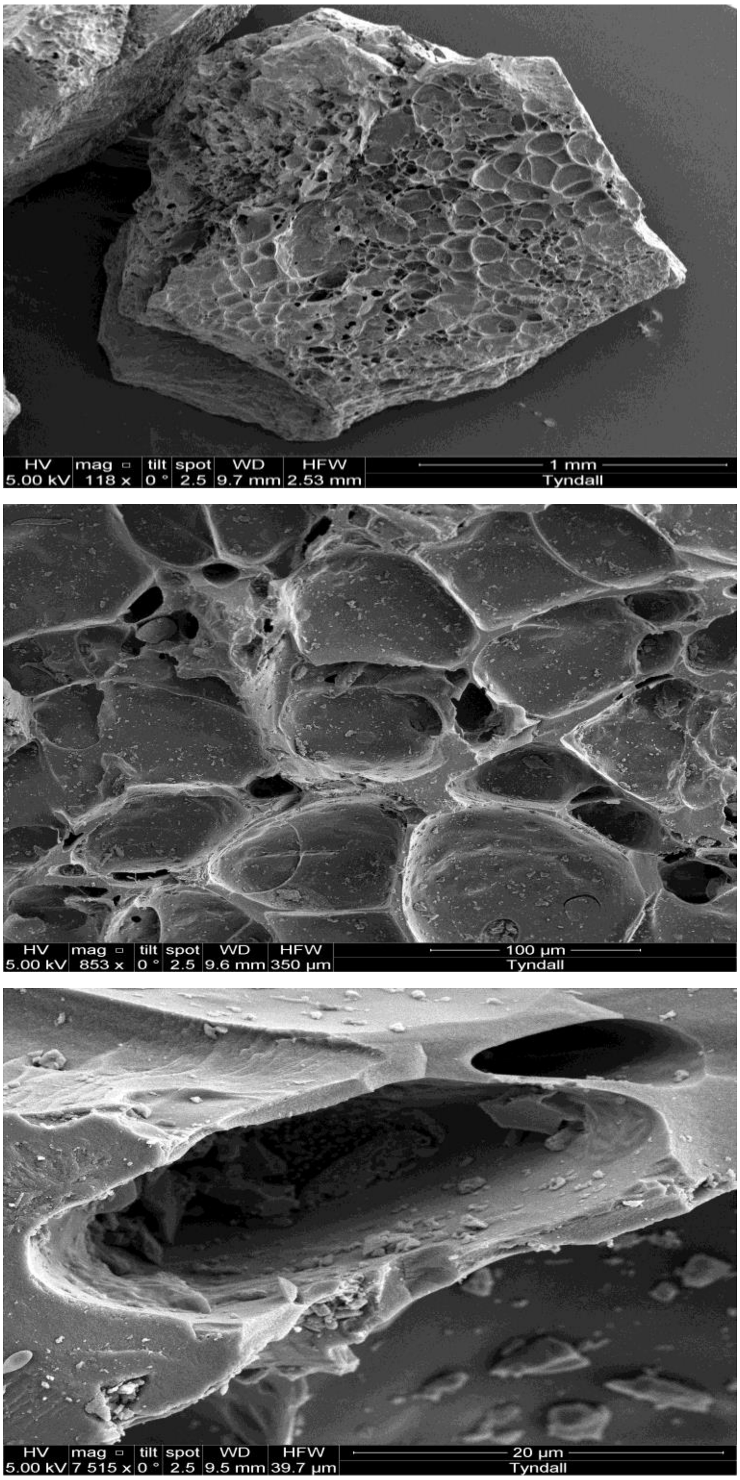


**Figure 4-1: A granule of AC as seen with SEM at 5kV and magnification of 118x (top), Surface of granule of AC at 853x magnification (middle)and SEM image of a macropore of AC at 7515x magnification (bottom)**

Energy-dispersive X-ray spectroscopy (EDX) was also performed on the AC in order to make a comparison to the composite. Figure 4-2 shows elemental peaks of C (carbon), Au (Gold), and Cl (chlorine). The largest peak corresponds to carbon which is to be expected. The gold peaks result from the sample preparation, where the powdered sample is sputtered in gold in order to ionise the surface for imaging. The chlorine peaks correspond to the target analyte 2,4-D as the AC used for this image was taken from an 2,4-D adsorption experiment with AC.

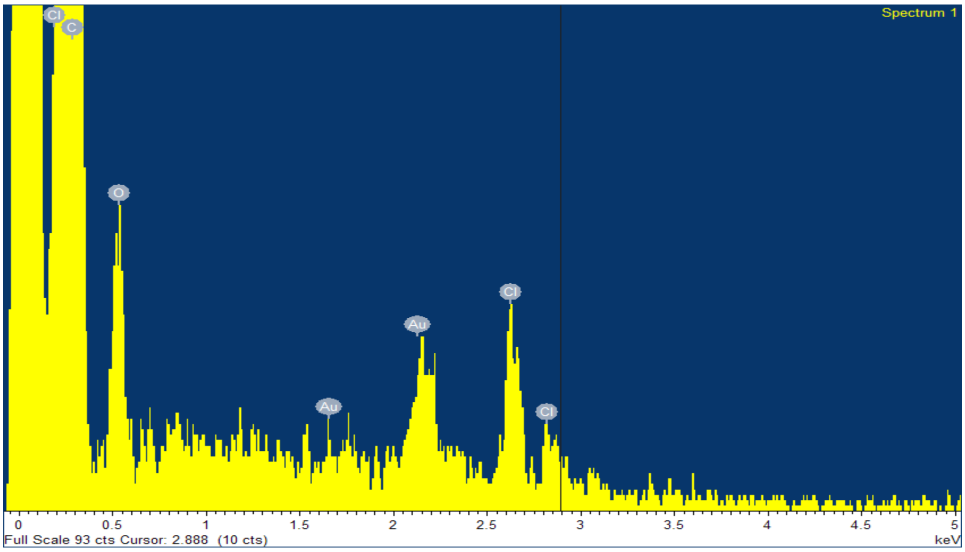


**Figure 4-2: EDX elemental analysis of AC**

The prepared composite samples were also analysed by SEM. Composite images and activated carbon images were compared (Figure 4-3 and Figure 4-4). The major difference between the two figures shown in Figure 4-4 is the presence of a $TiO_2$ coating on the surface of the AC.

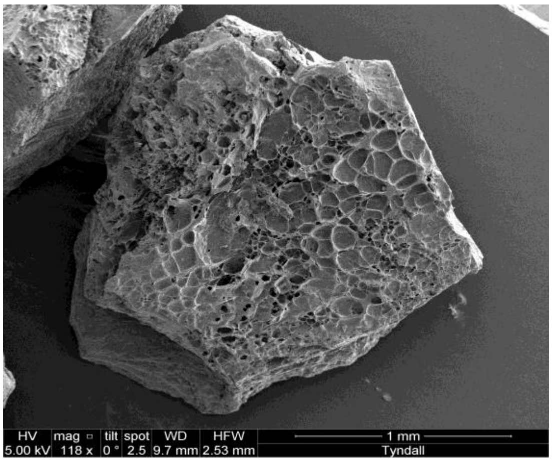


**Figure 4-3: AC at 118 magnification**

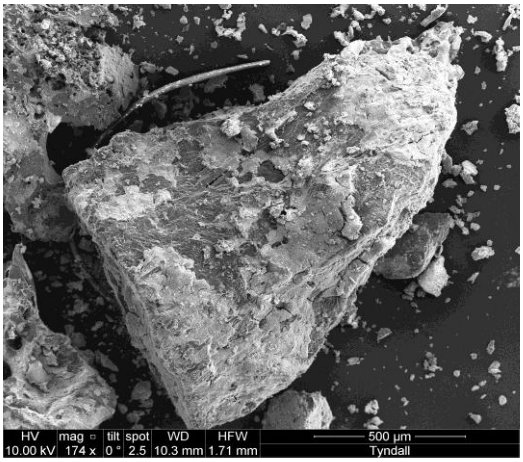
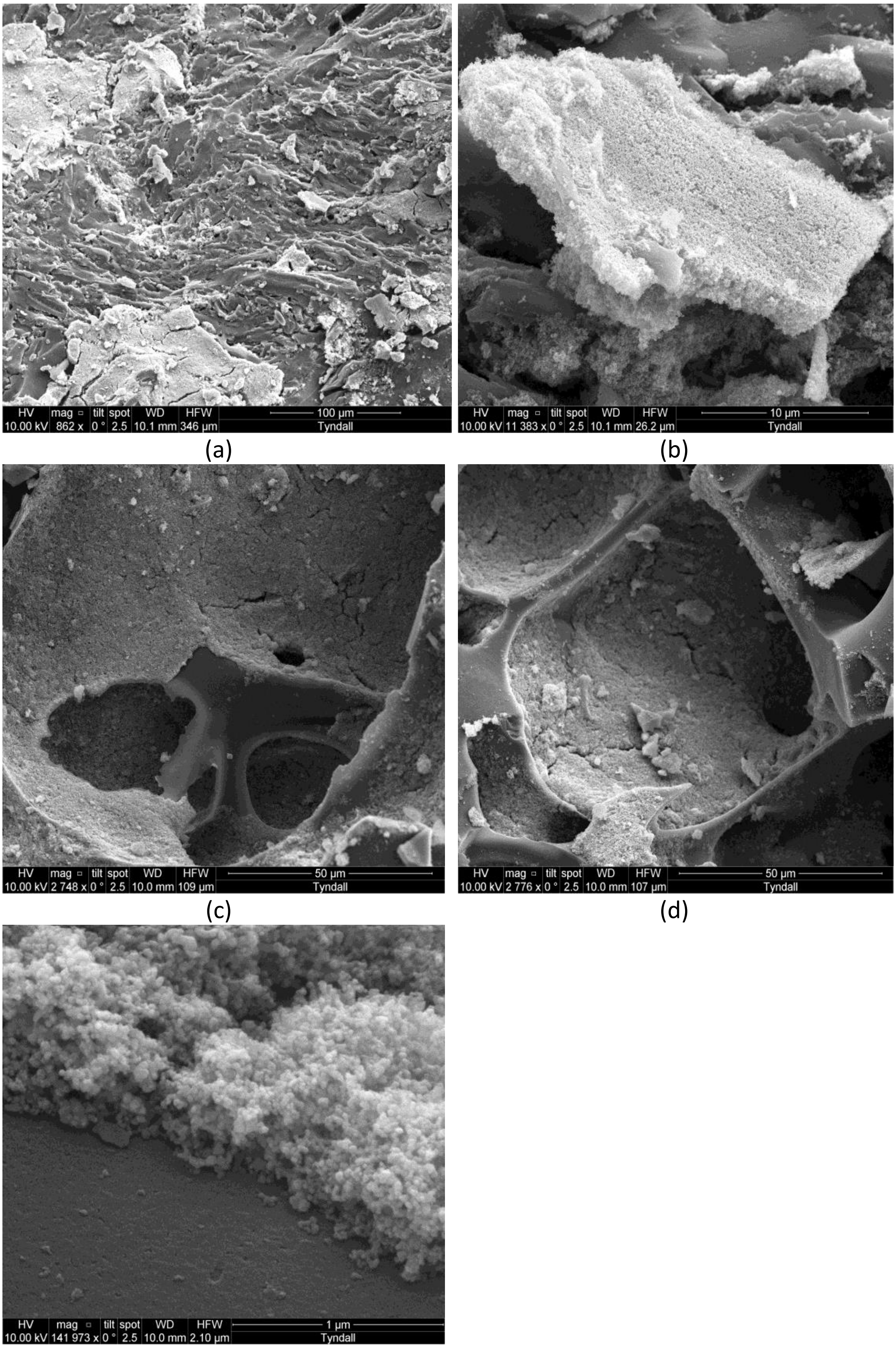


**Figure 4-4: AC/$TiO_2$ composite at 174 magnification**

When the SEM images of the composite are magnified further, it can be seen that $TiO_2$ is not evenly coated on the surface (Figure 4-5). $TiO_2$ is scattered in large aggregates (Figure 4-5(b)). It was suspected that the method of preparation was responsible for the aggregating of $TiO_2$. To investigate this phenomenon further, another batch of composite was made using the same method but was washed more thoroughly to remove excess $TiO_2$ from the surface. The resulting image of the new composite is shown in Figure 4-5(c). This composite showed a much more even distribution of $TiO_2$. Although there were some gaps on the surface most areas were covered. This image clearly distinguishes the areas coated with $TiO_2$ with those that are not. Figure 4-5(d) shows that the $TiO_2$ has penetrated into the mesopores of the AC. The SEM was also able to show the edge of the contact surface between $TiO_2$ and AC (Figure 4-5 (e)).



(a) (b)

(c) (d)

(e)

**Figure 4-5: (a) Composite at 862 magnification, (b) Aggregate of $TiO_2$ on the surface of AC at 11383 magnification, (c) Composite batch 2 at 2748 magnification (d) Composite batch 2 at 2776 magnification & (e) Edge of AC-$TiO_2$ interface on composite at 141973 magnification**

EDX analysis was also performed on both the original and new composite (with extra washing). Results are shown below in Figure 4-6. The analysis shows that there is a large peak for titanium indicating the presence of $TiO_2$ on the surface of the AC. This analysis also demonstrates that there is a large quantity of titanium in the sample as the carbon peaks (seen below in red) from the AC sample are masked by the surface titanium in the composite. The EDX results prove that titanium is present in the composite. These results compare to those in another study (Keane 2013) where percentage weight of titanium was determined to be 11.91 %.

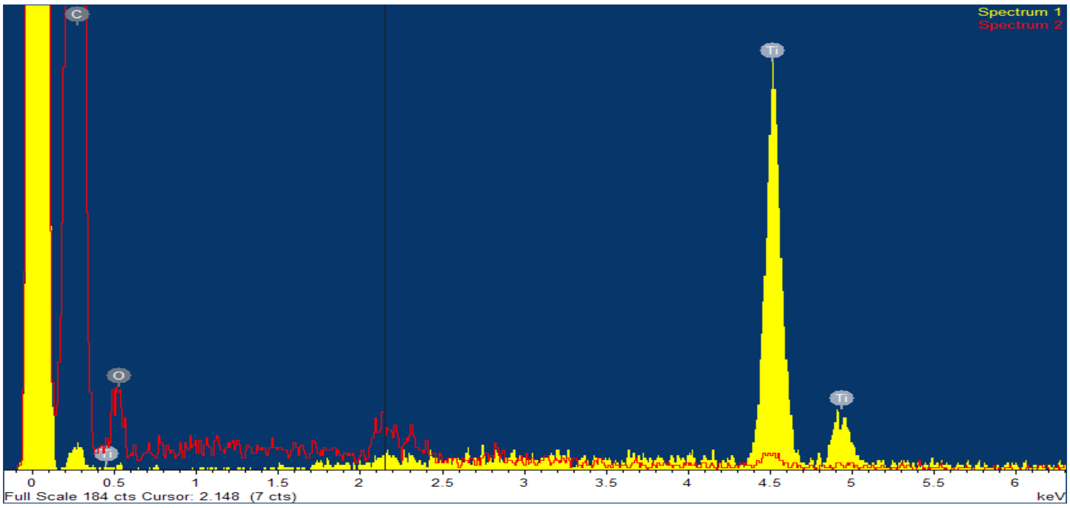


**Figure 4-6: EDX elemental analysis of composite (Spectrum one yellow) -spectrum two (red) = AC**

## 4.4. Sorption studies

Sorption studies were conducted in order to evaluate the adsorption capacity of the analytes to the activated carbon and to the AC/$TiO_2$ composite (10 % $TiO_2$). Aquasorb 2000 has moderate adsorption capacity, large grain size allowing easy liquid-solid separation and higher photocatalytic activity.

Equilibrium studies were first carried out with both MCPA and 2,4-D in order to determine the time it takes to reach equilibrium. Equilibrium can be defined as the reaching of a residual liquid-phase concentration of the solute that will not change with increasing time (Sontheimer, Crittenden and Scott Sommers 1988). In other words equilibrium was reached once the solution concentration remained constant with time. Figure 4-7 shows that both target analytes adsorb to AC at the same rate. Equilibrium was reached at 42 hr (2520 min). For the composite, the adsorption of analytes took 48 hr (2880 min) ( Figure **4-8**). Therefore it was decided to keep the equilibrium time constant for both AC and composite at 48 hr.

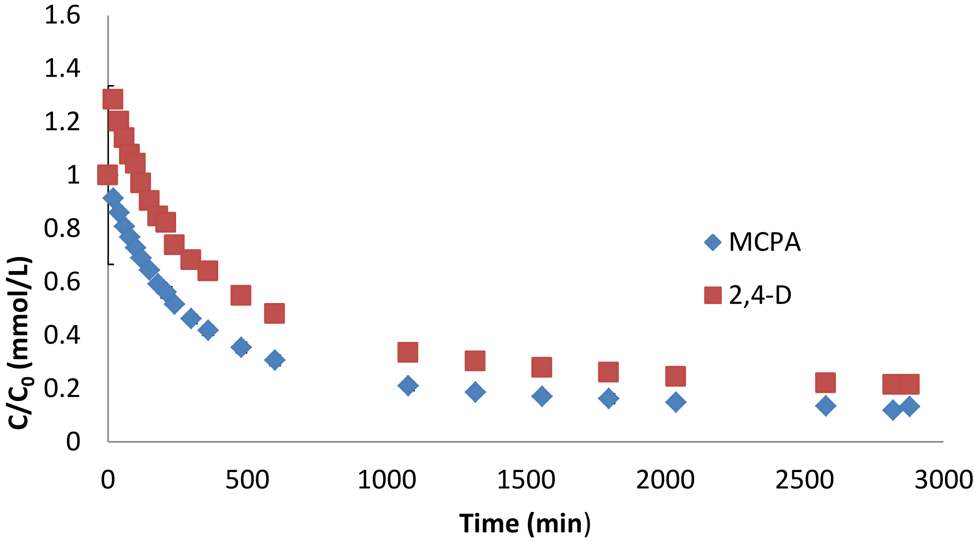


**Figure 4-7: Adsorption of 2,4-D and MCPA onto AC with time**

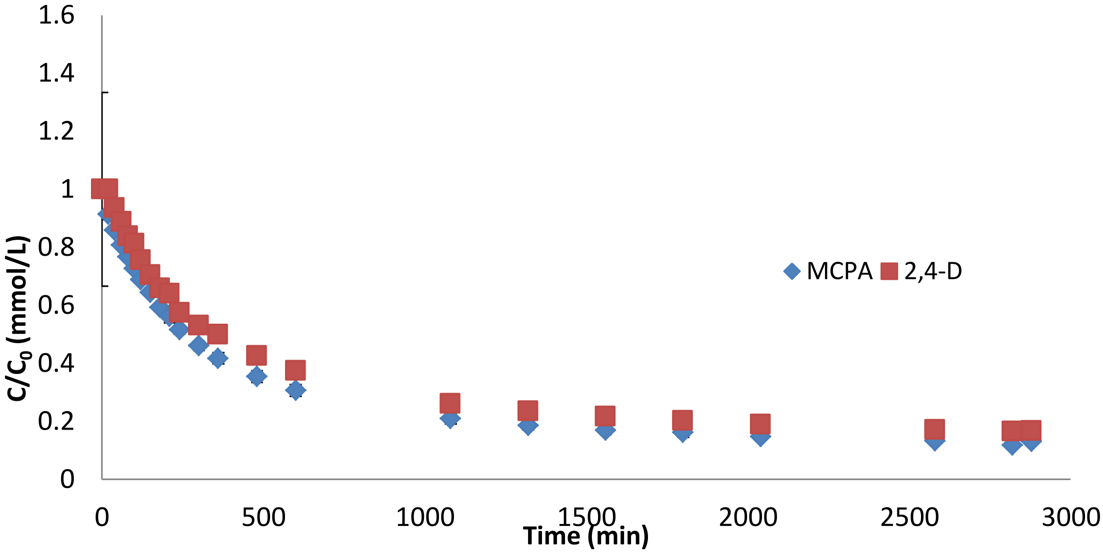


**Figure 4-8: Adsorption of 2,4-D and MCPA onto composite with time**

Batch adsorption studies or isotherms were then conducted to quantify adsorption of analytes onto both the AC and the composite. Isotherms were conducted as outlined in 3.2.2. The isotherm results (Figure 4-9, Figure 4-10) are in line with those seen in published literature (Chingombe, Saha and Wakeman 2006) and in research conducted within this research group (Engels 2012). MCPA adsorbs more efficiently and at faster rate than 2,4-D. For MCPA at an initial concentration of 0.6 mmol/l, there is a 76 % adsorption onto AC but for 2,4-D at the same initial concentration there is only 63 % adsorption onto AC. This difference may be attributed to the physiochemical properties of the analytes in particular the partition coefficient (Log P). MCPA has a log P value of 2.75 at pH1 whereas 2,4-D has a log P value of 2.58-3.83 at the same pH.

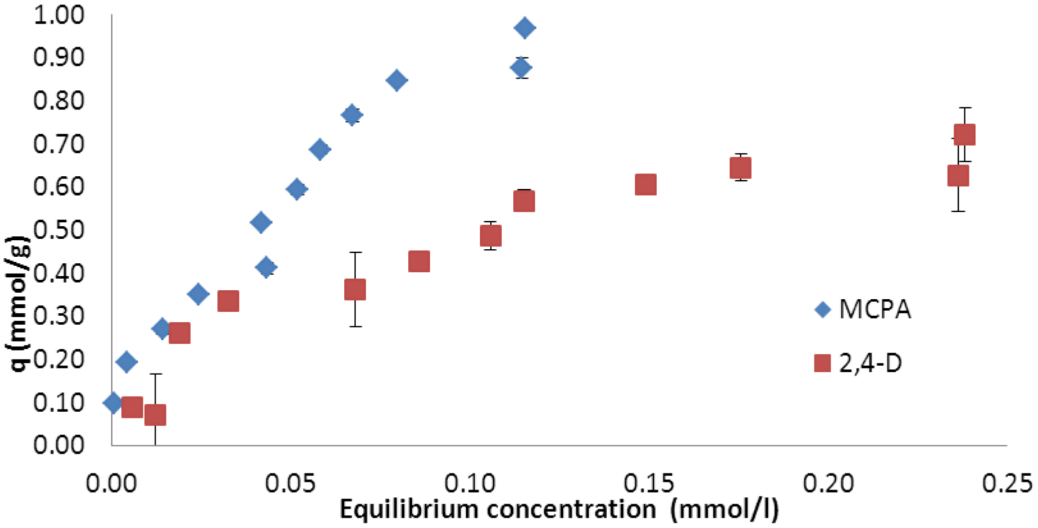


**Figure 4-9: Isotherms of 2,4-D and MCPA onto AC**

The analytes adsorption onto the AC/$TiO_2$ composite (Figure 4-10) shows a different adsorption pattern than that seen for AC (Figure 4-9). For most concentrations there is an overall increase in adsorption when compared to AC. Both 2,4-D and MCPA are adsorbed in equivalent manners to the AC/$TiO_2$ composite with neither pesticide having a larger adsorption capacity than the other.

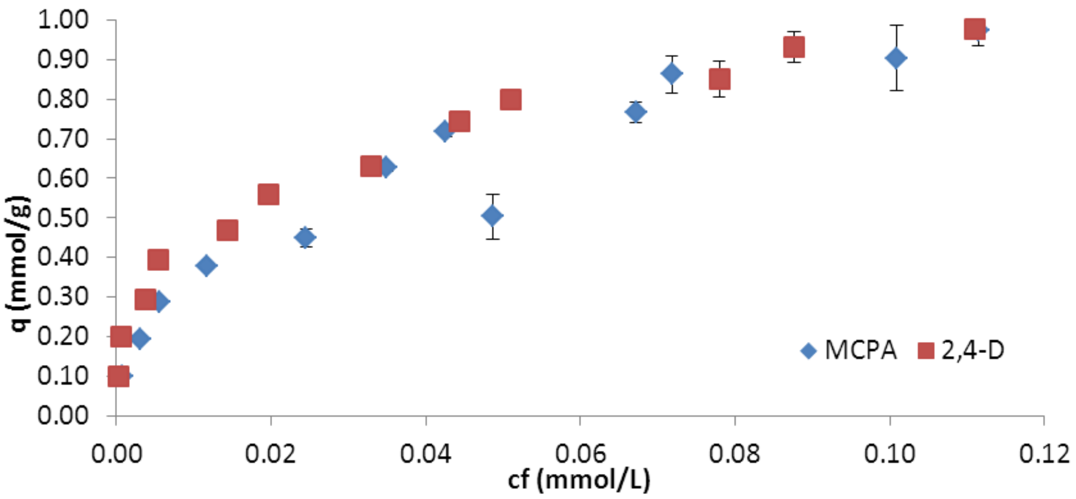


Figure 4-10: Isotherms of 2,4-D and MCPA onto composite

Isotherms were also conducted on $TiO_2$ but results varied considerably between replicate experiments and very little adsorption was noted (average of 50 % adsorption overall but at high concentrations of analytes, 0.6 mmol/l (<30 % adsorption). The powdered form of the $TiO_2$ made it difficult to weigh it accurately and at higher concentrations $TiO_2$ particles began to agglomerate.

### 4.4.1. Adsorption modelling

Isotherm data must be described by a mathematical model in order to quantify adsorption (Sontheimer, Crittenden and Scott Sommers 1988). This study investigated four of the most commonly used models; Langmuir, Freundlich, Toth and Redlich -Petterson.

The Langmuir model (eqn 3.1 section 3.3.5), assumes uniform energies of adsorption on the adsorbent surface. It also assumes a monolayer surface coverage. It was derived from kinetic considerations and the thermodynamics of adsorption. AC is not uniform so it is probable that energies of adsorption are not the same for all sites. Therefore it is likely that this model is not applicable (Sontheimer, Crittenden and Scott Sommers 1988).

The Freundlich model (eqn 3.2 section 3.3.5) is derived from observation or experimentation and assumes the adsorbent is non-uniform and the distribution of the sites with different energies of adsorption follow an exponential relationship. In most cases this model is better suited to describe aqueous phase adsorption than Langmuir (Sontheimer, Crittenden and Scott Sommers 1988).

The Toth model (eqn 3.4 section 3.3.5) is a mixture of both the Langmuir and Freundlich models. Two parameters are added to the equation making it a three parameter equation. This model assumes both a heterogeneous and homogenous surface exists (Sontheimer, Crittenden and Scott Sommers 1988).

The Redlich-Peterson model (eqn 3.3 section 3.3.5) is also a three parameter model. It converges to Henry's Law (At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid). This model is used for representing adsorption equilibrium over a wide concentration range, and can be applied in either homogeneous or heterogeneous systems due to its versatility (Piccin, Dotto and Pinto 2001) .

Figure 4-11 and Figure 4-12 show the mathematical modelling of MCPA and 2,4-D adsorption onto AC respectively. Figure 4-13 and Figure 4-14 show the modelling of MCPA and 2,4-D adsorption onto the AC/$TiO_2$ composite respectively.

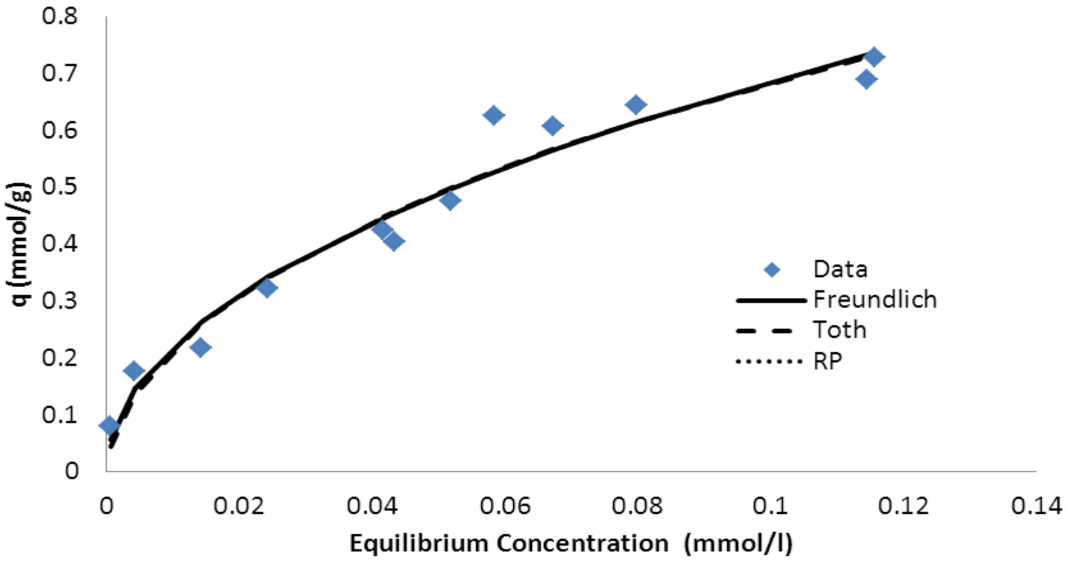


Figure 4-11: Mathematical modelling of MCPA adsorption onto AC

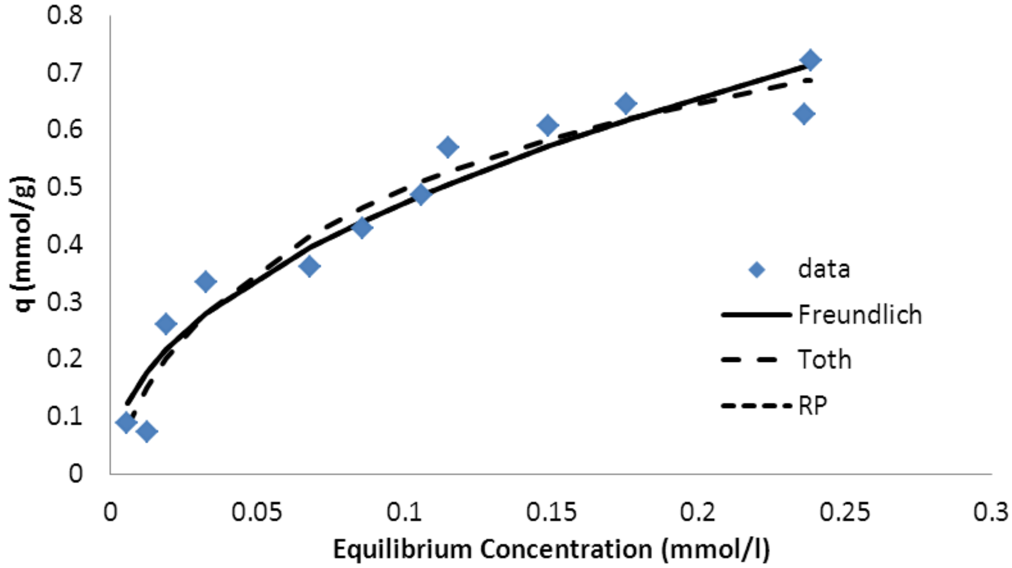


Figure 4-12: Mathematical modelling of 2,4-D adsorption onto AC

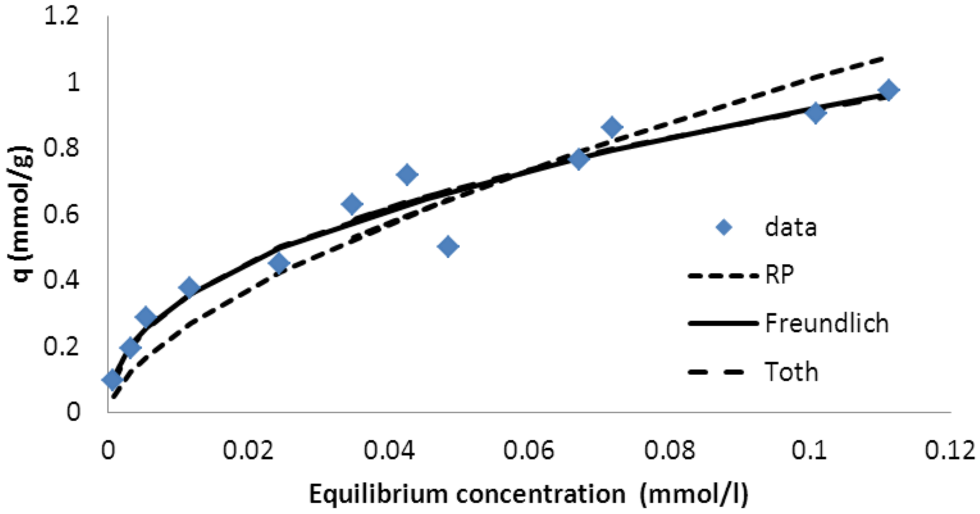


Figure 4-13: Mathematical modelling of MCPA adsorption onto composite

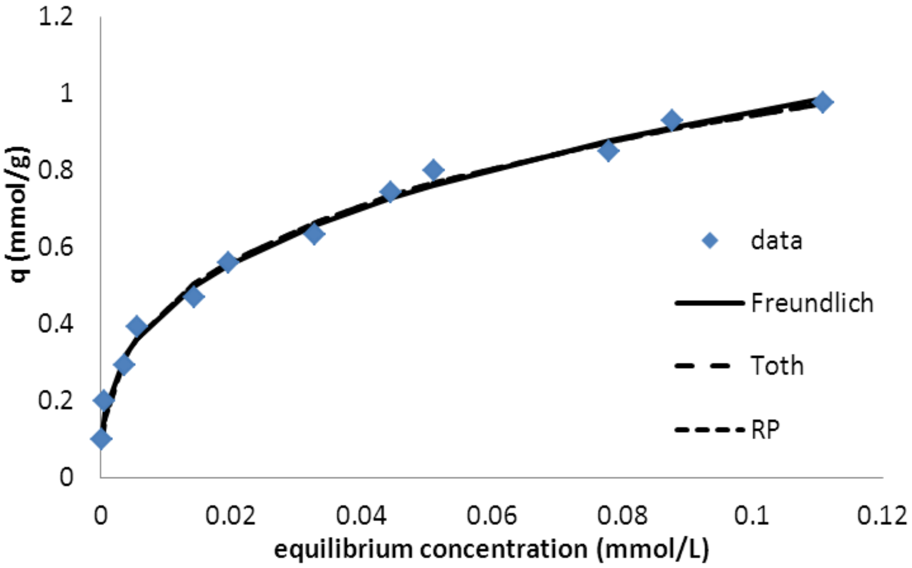


Figure 4-14: Mathematical modelling of 2,4-D adsorption onto composite

It is difficult to decipher the difference between models visually so statistical analysis was performed. Statistical results are shown in Table 4-1. This table shows that for all the mathematical models the error is larger with adsorption to AC than to the composite. The largest percentage absolute error of 22.2 % is for 2,4-D with AC for both the Freundlich and Redlich-Peterson models. This indicates that $TiO_2$ is aiding the adsorption onto AC. This is thought to be due to the $TiO_2$ adding surface area to the AC surface and therefore increasing the number of adsorption sites (Jamil *et al*. 2012).

Freundlich results from Engels *et al*. (2012) are compared to parameters in Table 4-1 for 2,4-D –AC and MCPA –AC. $K_f$ values for Engels 2012 are 1.85 and 2.32 for MCPA-AC and 2,4-D-AC respectively. Engels used a much shorter equilibrium time of 16 hr compared to this 48 hr study, which means that the both 2,4-D and MCPA may not have been in equilibrium at the stage of sampling in Engels study.

**Table 4-1: Adsorption Isotherm parameters for adsorption of target analytes on AC and composite**

| Isotherm models | Analyte - adsorbent | | | |
|---|---|---|---|---|
| | **MCPA-AC** | **MCPA-Comp** | **2,4-D- AC** | **2,4-D-comp** |
| | | **Freundlich** | | |
| kf | 2.1177 | 2.5128 | 1.4027 | 2.0576 |
| n | 0.4900 | 0.4368 | 0.4713 | 0.3338 |
| SSE | 0.0224 | 0.0463 | 0.0314 | 0.0072 |
| RMSE | 0.1401 | 0.1626 | 0.1592 | 0.0873 |
| AE | 11.1430 | 8.4529 | 22.1791 | 6.2004 |
| | | **Toth** | | |
| Alpha | 1.3818 | 1.7548 | 4.7558 | 2.7713 |
| Beta | 0.0942 | 0.0894 | 0.5568 | 0.0839 |
| Qm | 19144.8 | 186981.8 | 22.52 | 13540613.5 |
| SSE | 0.0229 | 0.0473 | 0.0249 | 0.0082 |
| RMSE | 0.1515 | 0.1720 | 0.1640 | 0.0872 |
| AE | 12.5592 | 8.4929 | 17.4197 | 5.1935 |
| | | **Redlich-Peterson** | | |
| k | 2.5951 | 2.7529 | 2.0759 | 2.5577 |
| b | 0.2254 | 0.0956 | 0.4799 | 0.2430 |
| beta | 0.5100 | 0.5632 | 0.5287 | 0.6662 |
| SSE | 0.0224 | 0.0463 | 0.0314 | 0.0072 |
| RMSE | 0.1477 | 0.1714 | 0.1678 | 0.0920 |
| AE | 11.1432 | 8.4528 | 22.1789 | 6.2002 |

### 4.4.2. Kinetic Modelling

To investigate the adsorption of the target analytes further, kinetic studies were conducted. Kinetic experiments determine the removal of target analytes over time. The kinetic mechanism is important in adsorption processes because it determines the uptake rate and the time to completion of the entire process (Basha *et al.* 2010). It can also help to determine the reaction mechanism and establish the concentration needed to be most effective at adsorbing pollutants. There are numerous kinetic models available to describe the adsorption process but this study will use two of the most common ones, pseudo first-order and pseudo-second-order. The model equations along with kinetic and statistical parameters are listed in Table 4-2.

**Table 4-2: Kinetic parameters for 2,4-D and MCPA adsorption onto AC and AC/$TiO_2$ composites**

| | | Adsorbents | | | |
|---|---|---|---|---|---|
| | | **MCPA** | | **2,4-D** | |
| **Models** | | AC | AC/$TiO_2$ comp | AC | AC/$TiO_2$ comp |
| Experimental sorption capacity/mg $g^{-1}$ | | | | | |
| **Pseudo-first-order** | $q_t = q_e[1 - \exp(-k_1 t)]$ | | | | |
| $k1/\mathrm{min}^{-1}$ | | 0.007 | 0.003 | 0.003 | 0.004 |
| $qe$/mg $g^{-1}$ | | 162.771 | 173.915 | 242.636 | 229.997 |
| *SE* | | 16.629 | 5.903 | 12.5446 | 21.168 |
| SSE | | 4424.27 | 731.756 | 3304.7 | 9409.35 |
| **Pseudo-second-order** | $q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$ | | | | |
| $qe$/mg $g^{-1}$ | | 179.439 | 205.445 | 254.722 | 239.190 |
| $k2$/g $mg^{-1}$ $min^{-1}$ | | $5.04 \times 10^{-5}$ | $1.81 \times 10^{-5}$ | $1.53 \times 10^{-5}$ | $1.77 \times 10^{-5}$ |
| $h$/mg $g^{-1}$ $min^{-1}$ | | 1.623 | 0.765 | 0.993 | 1.010 |
| *SE* | | 14.283 | 1.702 | 9.361 | 17.205 |
| *SSE* | | 3263.94 | 60.825 | 1840.17 | 6215.96 |

The experimental and predicted pseudo-first order kinetic data for MCPA adsorption to AC and AC/$TiO_2$ are shown in Figure 4-15 and the pseudo-second order data MCPA is shown in Figure 4-16. The pseudo first and second order data for 2,4-D is shown in Figure 4-17 and Figure 4-18 respectively. Overall both the pseudo first order and second order fit well to the experimental data at lower times but after 600 min (10 hr) the predicted values do not fit well to the dataset. After 600 min adsorption appears to slow down with at least 50 % of the initial concentration being adsorbed at this point. The lowest SE values correspond to MCPA adsorption to AC/$TiO_2$ for both pseudo first (5.903) and second order (1.702). This corresponds to the adsorption isotherm data discussed in section 4.4 where it was determined that the AC/$TiO_2$ composite gave the most efficient adsorption. The good agreement between the experimental and predicted equilibrium sorption capacities confirm better fit to the pseudo-second order model.

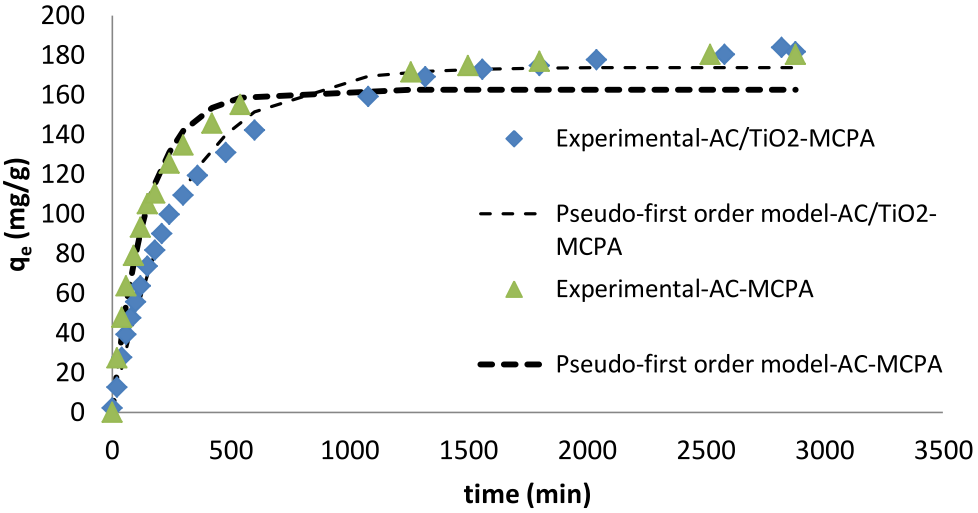


**Figure 4-15: Comparison of pseudo-first- order kinetic models of MCPA adsorption onto AC and AC/$TiO_2$**

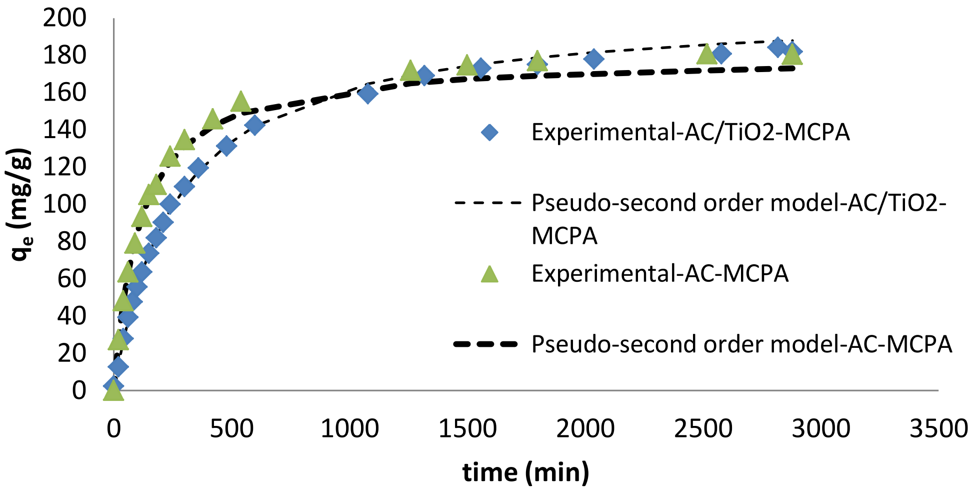


**Figure 4-16: Comparison of pseudo-second- order kinetic models of MCPA adsorption onto AC and AC/TiO$_2$**

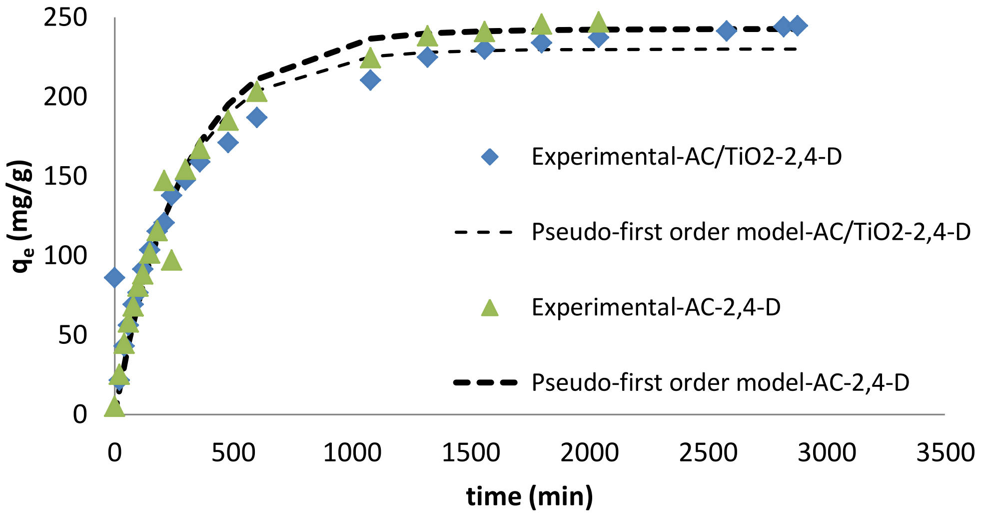


**Figure 4-17: Comparison of pseudo-first- order kinetic models of 2,4-D adsorption onto AC and AC/TiO$_2$**

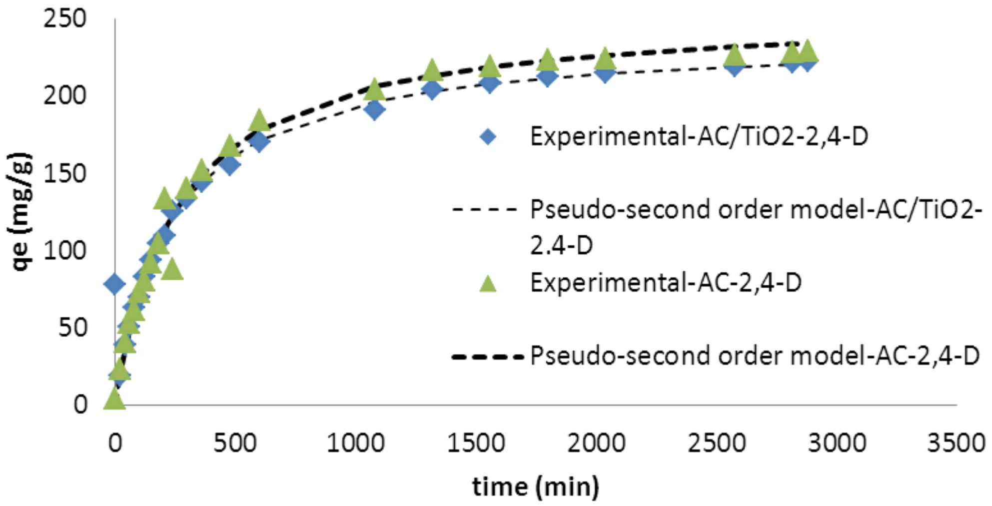


**Figure 4-18: Comparison of pseudo-second- order kinetic models of 2,4-D adsorption onto AC and AC/TiO$_2$**

## 4.5. AC/TiO$_2$ Composite Photodegradation Results

### 4.5.1. Composite Optimisation Parameters

In this section, the photodegradation capacity of the composite was investigated by placing solutions of target analytes in reactors that were exposed to UV and visible light irradiation. The systems needed to be optimised in order to achieve efficient removal of 2,4-D and MCPA from aqueous solutions. Parameters such as reactor volume, batch reproducibility, weight of composite, composition of composite, pH and initial concentration of analyte were investigated (Figure 4-19). Photodegradation experiments were plotted as $C/C_0$ versus time (concentration at time t divided by the initial concentration plotted against time).

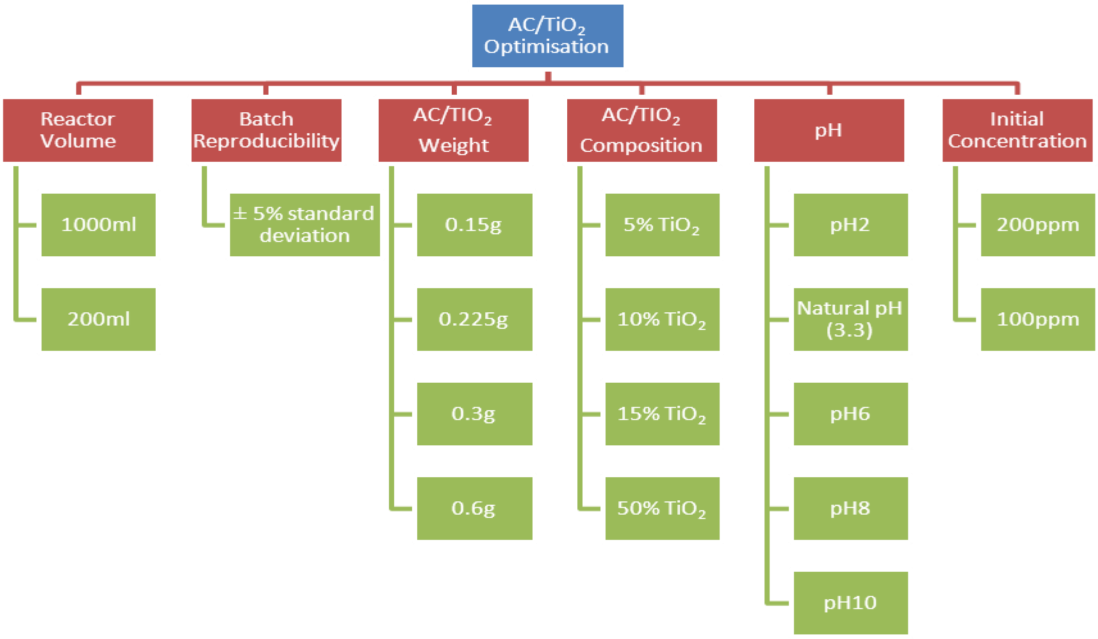


**Figure 4-19: Flow chart showing the AC/$TiO_2$ optimisation parameters investigated**

### Reactor Volume

Two reactors with volumes of 200 mL and 1000 mL, were investigated (Figure 4-20) [The light is switched on at the time indicated in all graphs. Prior to this time it is dark adsorption].

A 10 % composite was tested using both reactor volumes with an initial concentration of 0.3 mmol/L of MCPA. The conditions of 10 % composite and 0.5 mM of MCPA were selected based on previous optimisation studies carried out within the research group on pharmaceuticals which showed the optimum conditions for these studies to be 0.3 g of 10 % $TiO_2$ composite (Keane 2013). These conditions were then further optimised by looking at individual parameters outlined in the sections below. As both reactor volumes showed equivalent results, the 200 mL reactor was selected as this would result in less chlorinated waste being generated for disposal.

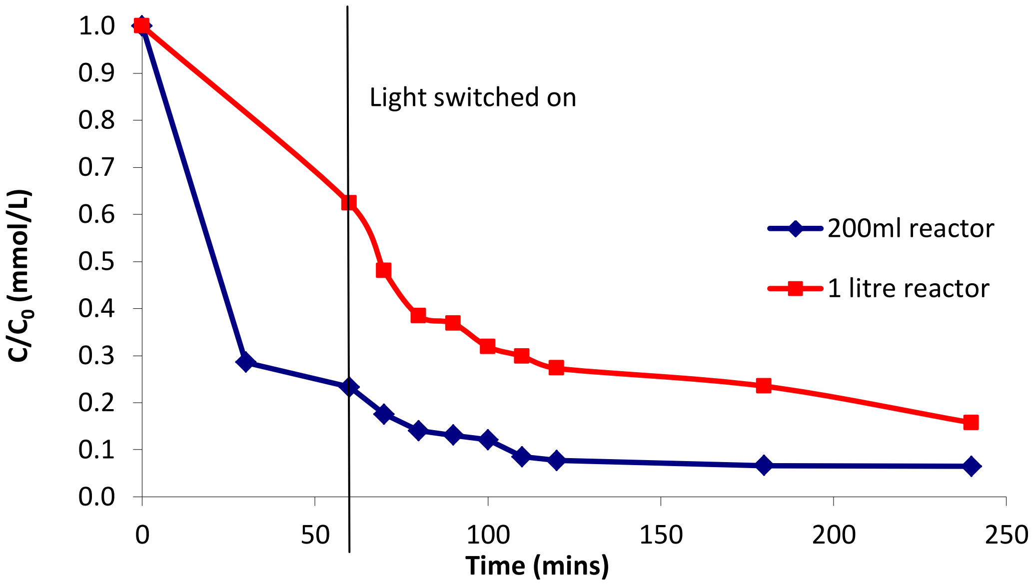


**Figure 4-20: Reactor volumes used for photodegradation of MCPA**

### 4.5.1.1. Batch reproducibility

To determine consistent photodegradation results between different batches of the same composite, the reproducibility was investigated (Figure 4-21). Consistent results were obtained with a maximum standard deviation of 2.6 % (Table 4-3) which is below the acceptable level of 5 %.

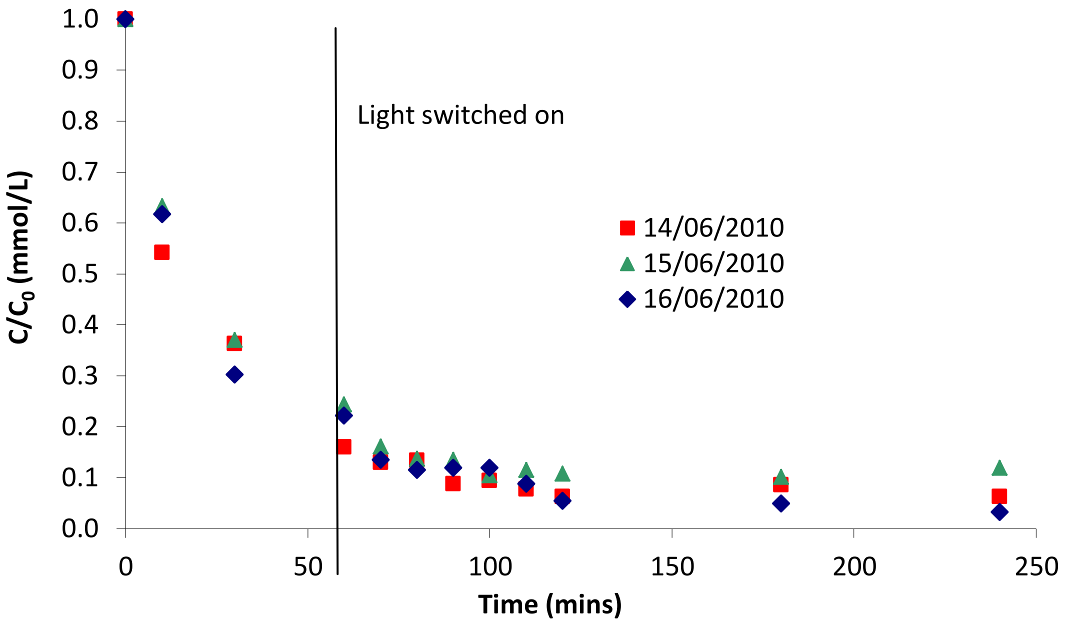


**Figure 4-21: Reproducibility of 10% composite batches used to degrade MCPA**

**Table 4-3: Standard deviation of the degradation of MCPA using same batch of 10% composite carried out on three consecutive days**

| Sample Time Intervals | Concentration (mM) Day 1 | Concentration (mM) Day 2 | Concentration (mM) Day 3 | Standard deviation |
|---|---|---|---|---|
| Initial Sample | 0.490 | 0.541 | 0.522 | 0.026 |
| Addition of AC | 0.365 | 0.342 | 0.322 | 0.022 |
| 30 min in Dark | 0.178 | 0.200 | 0.158 | 0.021 |
| 60min in Dark | 0.078 | 0.131 | 0.116 | 0.027 |
| 10min in light | 0.063 | 0.087 | 0.070 | 0.012 |
| 20min in light | 0.065 | 0.074 | 0.060 | 0.007 |
| 30min in light | 0.043 | 0.073 | 0.062 | 0.015 |
| 40min in light | 0.046 | 0.057 | 0.062 | 0.008 |
| 50min in light | 0.038 | 0.062 | 0.046 | 0.012 |
| 60min in light | 0.031 | 0.058 | 0.028 | 0.017 |
| 120min in light | 0.042 | 0.055 | 0.025 | 0.015 |
| 180min in light | 0.031 | 0.064 | 0.017 | 0.024 |

### Weight of composite

In order to optimise the weight of the composite to be used in the photodegradation experiments, the following weights of composite were tested for the photodegradation of MCPA; 0.15 g, 0.225 g, 0.3 g and 0.6 g (Figure 4-22). The 0.3 g and 0.6 g showed the most efficient degradation with 96 % removal after 180 min of UV illumination. When using 0.15 g, the removal rate was 76 %, which makes it the least efficient of the weights investigated and it is the lowest weight used. 0.3 g was chosen as the optimum weight as 0.6 g worked as effectively but caused the reaction solution to become cloudy which may have affected both the stirring capacity of the system and the light penetration.

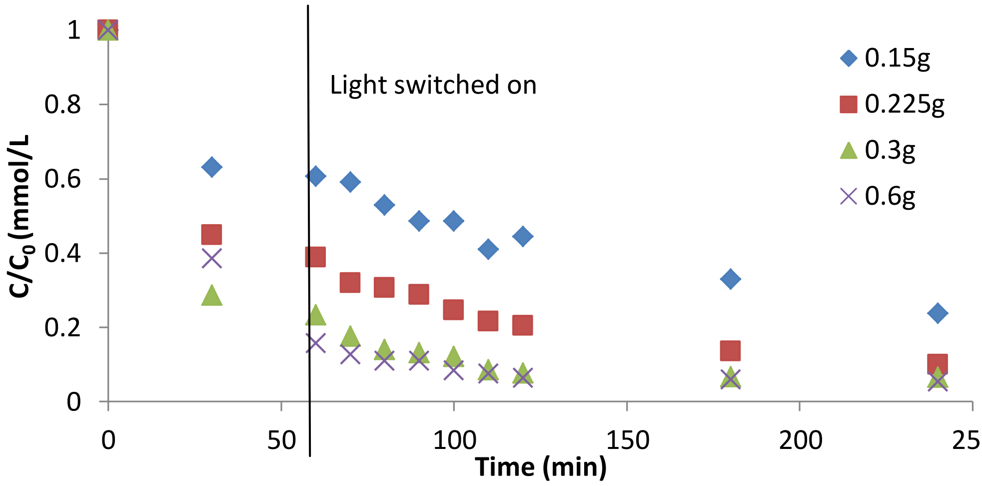


**Figure 4-22: Weight optimisation of 10% composite for the degradation of MCPA**

### Percentage of $TiO_2$ present in AC/$TiO_2$ composite

The following percentages of $TiO_2$ on AC were also investigated in order to optimise the photodegradation of MCPA; 5, 10, 15 and 50 % (Figure 4-23). The composite was prepared as described in section 4.2.

No significant difference is noted in the removal of MCPA between the different composites investigated. The 10 % composite shows a slight increase in degradation rate and gives 94 % removal of MCPA after 60 min of illumination. In contrast to this the 5 % composite gave 90 % removal after 60 min of illumination. The 10 % composite was then used in all further experiments.

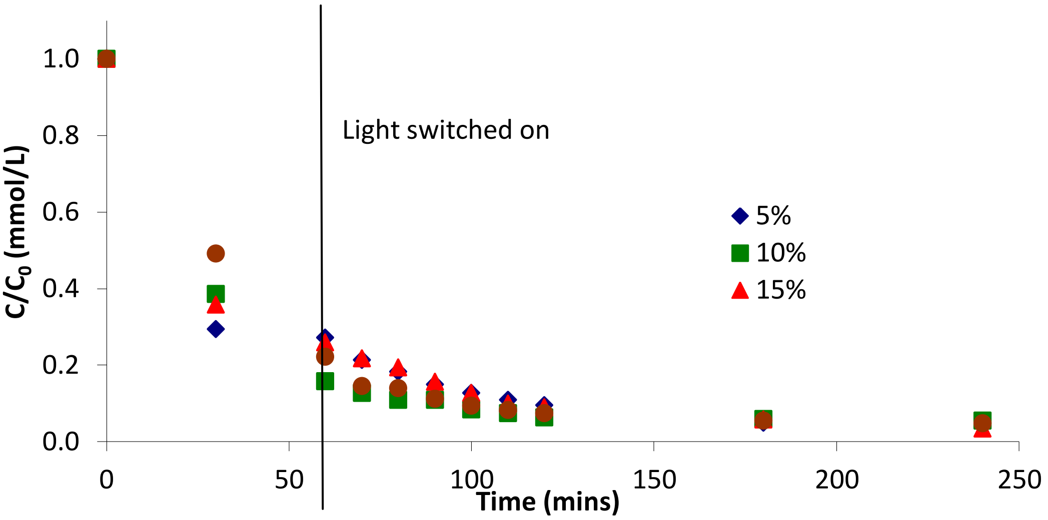


**Figure 4-23: Optimisation of percentage of $TiO_2$ contained in composite (MCPA).**

### pH studies

The effect of pH for the 10 % composite on the removal of MCPA was also investigated (Figure 4-24). The pH of the solution affects the analytes' adsorption and photodegradation. Adsorption onto AC was previously determined to be most effective at acidic pH's or pH values closest to the $pK_a$ of the analytes (Engels 2012). The $pK_a$ of 2,4-D is between 2.64 - 3.31 (at $25^0C$) and of MCPA is 3.07 (at $25^0C$) (Tomlin 1994). Previous workers have shown that photodegradation using $TiO_2$ was found to be most efficient at alkaline pH's (Modestov and Lev 1998). The following pHs 2, 3.3, 6, 8 and 10 were investigated for both analytes using the 10 % composites (Figure 4-25). For both analytes a similar trend was found. The natural pH (3.3) was found to be the most efficient for the removal of the analytes with 95 % removal of 2,4-D and 98 % removal of MCPA.

The point of zero charge of comparable composites is reported to be in the range 6.8–7.2 while the p*K*a of 2,4-D is 2.64 and of MCPA is 3.07 (Tomlin 1994, Gu *et al.* 2010). Accordingly, the composite surface is expected to be positively charged at pH < 7 and negatively charged at pH > 7. Furthermore, at pH 3.3 a percentage of both analytes would be expected to be in the neutral free acid form which is the least soluble form of the target analytes. From the Henderson Hasselbach equation a value of 4.57 is obtained for the conjugate base to acid ratio of 2,4-D.

It has been shown in the literature that the removal of 2,4-D increases with decrease of pH and that phenoxy acids showed increasing sorption with decreasing pH (Alam, Dikshit and Bandyophadyay 2002). At low pH, 2,4-D remains in the acid form (i.e., neutral) and at high pH, it is in the anionic form. As anions are less susceptible to sorption onto carbon, the maximum removal of 2,4-D at pH 3.3 was due to the affinity of AC for the neutral species. The same can be said for MCPA as its structure and physical-chemical properties are similar. The least efficient removal was found at pH 10 with a 68 % removal of 2,4-D and 65 % removal of MCPA (Modestov and Lev 1998).

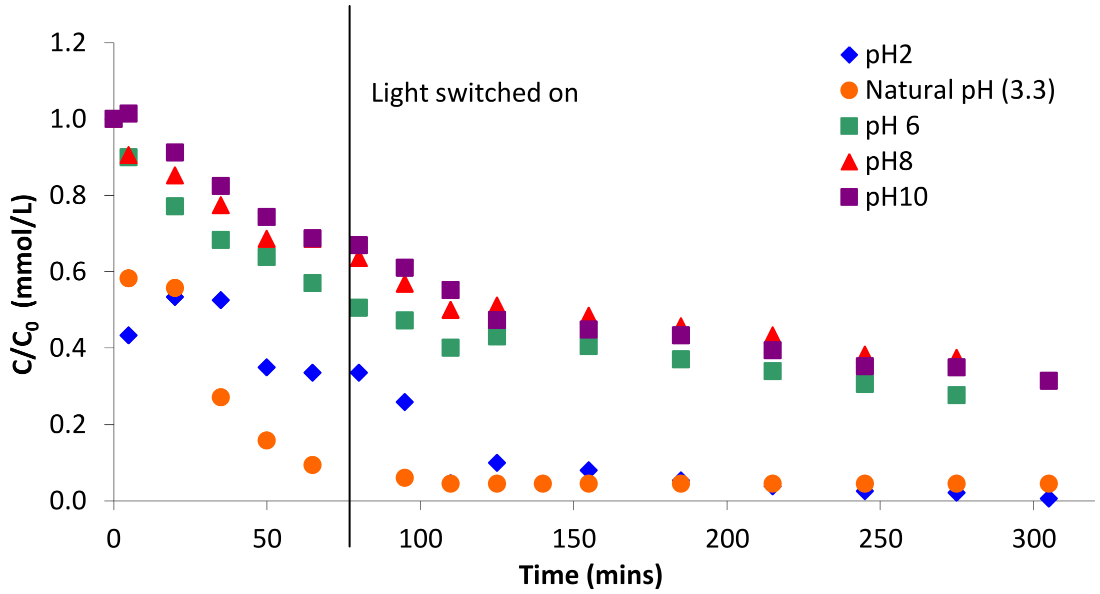


**Figure 4-24: effect of pH on composite with MCPA in the dark and with UV light (248 -579nm)**

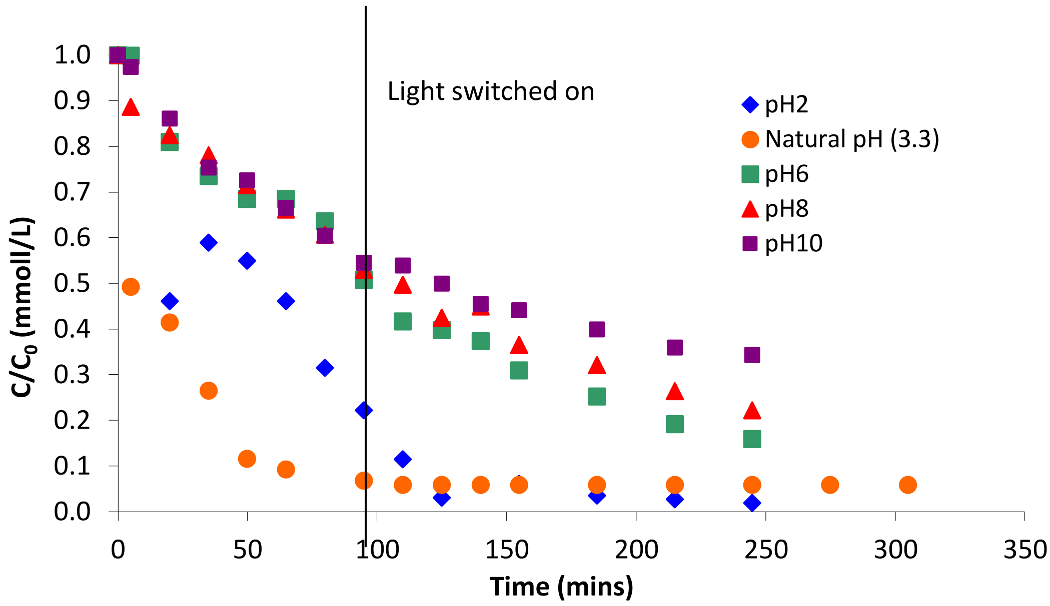


**Figure 4-25: effect of pH on composite with 2,4-D in the dark and with UV light (248 -579nm)**

### Initial Concentration of target analytes in solution

The initial concentration is an important value to consider. Both MPCA and 2,4-D are found in µg/l levels in Irish waters (EPA 2006). For photodegradation experiments 100 mg/L (0.5mM) solutions of the analytes were prepared. The initial concentrations of MCPA (100 mg/L and 200 mg/L) were compared (Figure 4-26). The graphs for both experiments showed similar trends, demonstrating that the initial concentration did not affect the rate of photodegradation of MCPA when 10 % composites were utilised.

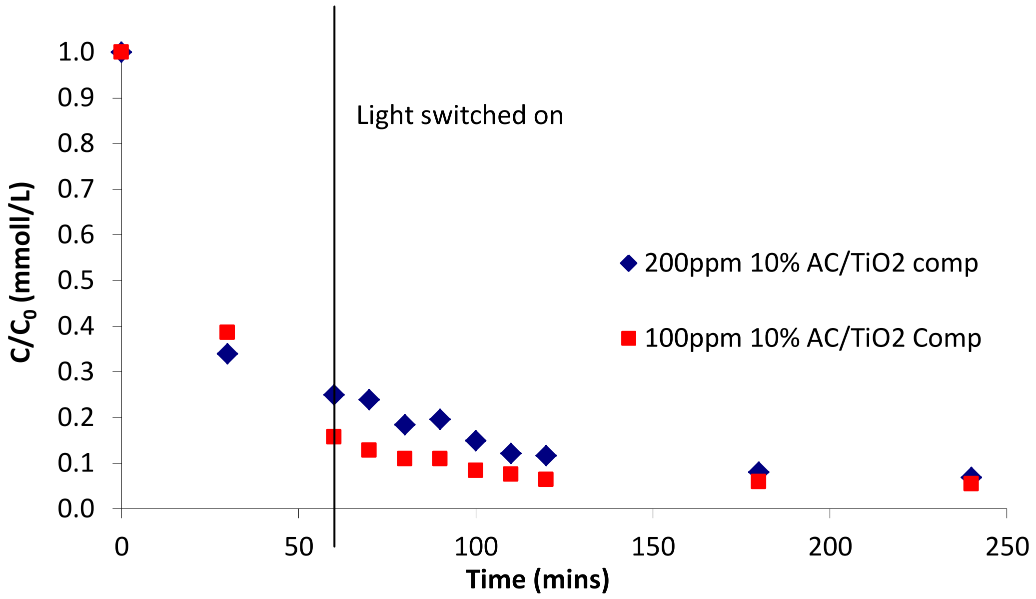


**Figure 4-26: 200ppm and 100ppm initial concentration of MCPA, 10 % composite, in the dark and UV light (248 -579nm)**

### 4.5.2. Analysis of photodegradation and adsorption processes of AC/$TiO_2$ composite

Once the parameters of the composite photodegradation were determined, controls were used to establish the effectiveness of the adsorption and photodegradation components of the composite. The control experiments investigated were;

1. Control experiments conducted in the dark
2. Experiments conducted with activated carbon instead of AC/$TiO_2$ composite
3. Experiments conducted with $TiO_2$ instead of the AC/$TiO_2$ composite and pH studies

**Dark vs. Light**

Experiments were performed as previously described in section 3.2.3 using 2,4-D as the analyte but without the presence of UV illumination. These results were then compared to an experiment that was conducted under UV light between 248 and 579nm (Figure 4-27). No significant difference was noted when the experiment was conducted with or without UV light. A maximum standard deviation of 3.7 % was found between the two experiments. It would imply that adsorption was the dominating mechanism for the removal of 2,4-D.

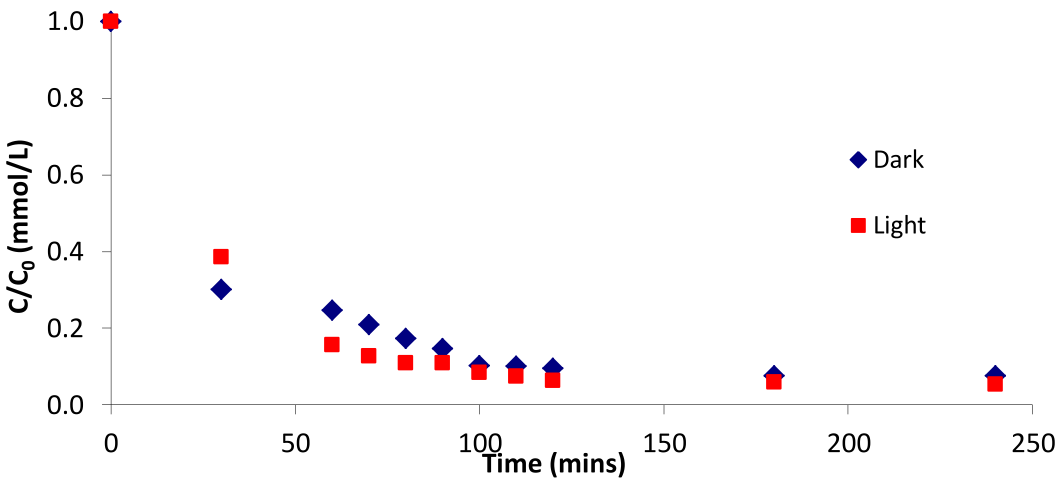


**Figure 4-27: Composite experiments conducted with and without UV light with MCPA as analyte**

**Activated Carbon**

Activated carbon controls were also carried out (Figure 4-28). 0.3 g (optimum weight of composite) of AC was placed in the reaction solution and the experiments were carried out in the dark and under UV illumination (248 -579 nm).

Both 2,4-D and MCPA showed similar adsorption patterns. When the AC controls are compared to the 10 % composite (Figure 4-29 and Figure 4-30) similar plots are observed indicating that adsorption is the dominating process occurring with the composite. As discussed in the sorption section (section 4.4) both the analytes adsorb strongly to activated carbon and so there is very little analyte left to degrade once the light is switched on.

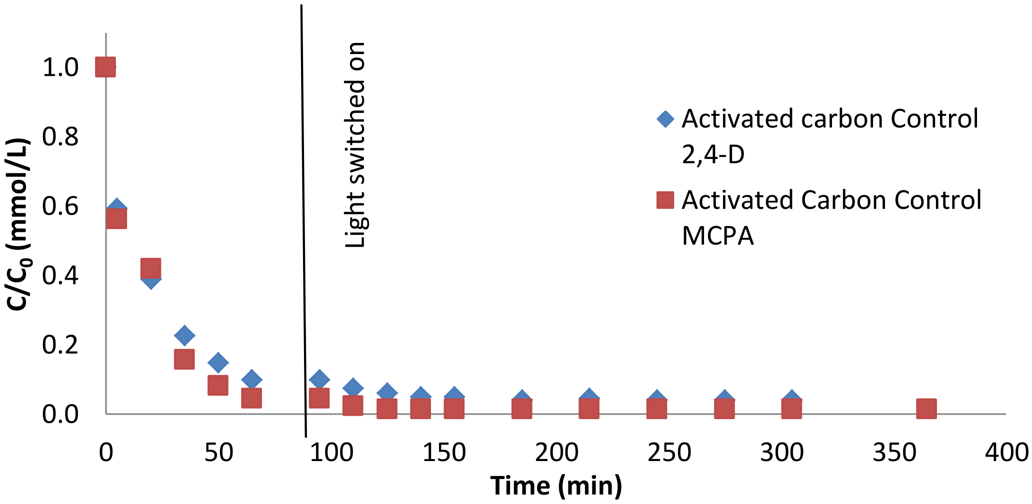


Figure 4-28: Activated Carbon controls for MCPA and 2,4-D

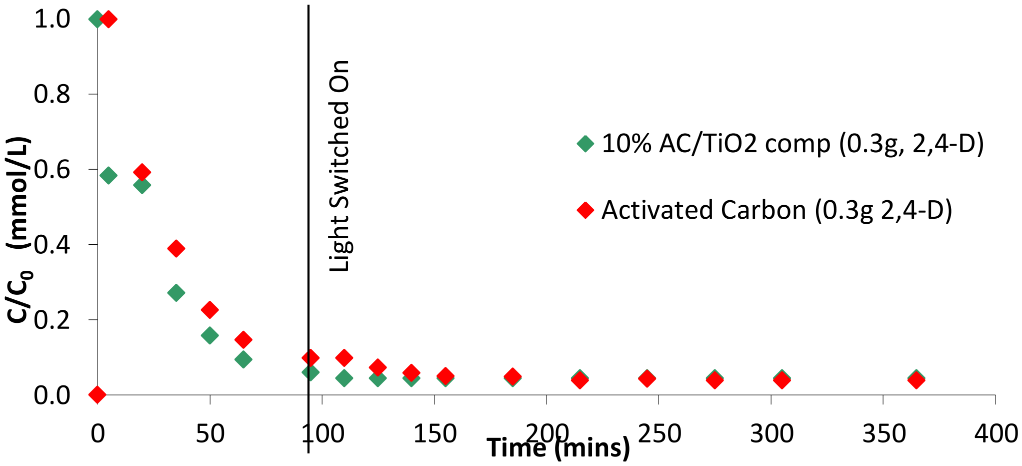


Figure 4-29: Activated Carbon Control compared to composite for 2,4-D photo degradation

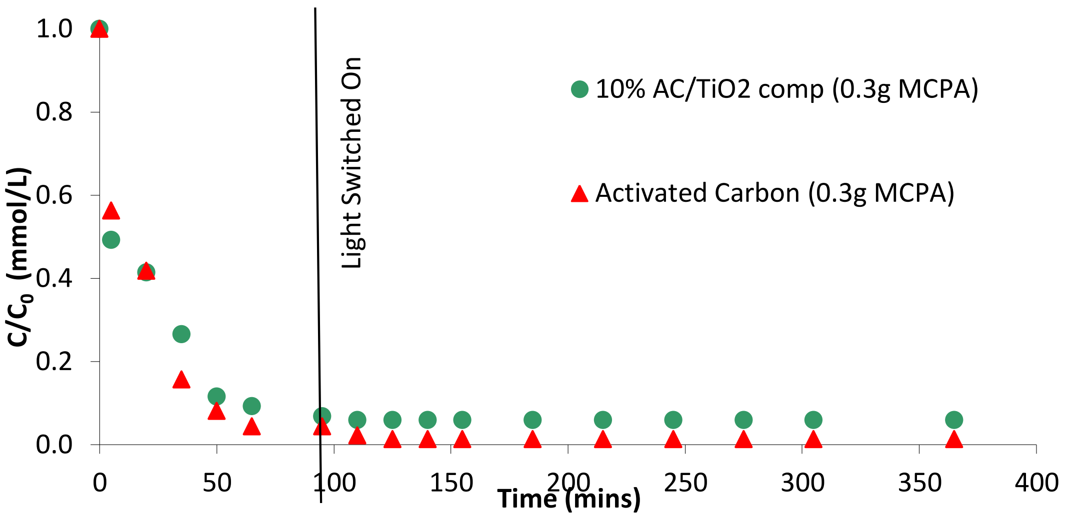


**Figure 4-30: Activated Carbon Control compared to composite for MCPA degradation**

**Titanium Dioxide**

Controls using $TiO_2$ were carried out to investigate the photodegradation ability of the composite (Figure 4-31 and Figure 4-32). These experiments were carried out using 0.3g of $TiO_2$ added to the reaction under the same conditions as all experiments as described in section 3.2.3.

The 2,4-D $TiO_2$ control (Figure 4-31) showed efficient degradation 50 % of 2,4-D was adsorbed in the dark, followed by 47 % photodegradation with UV irradiation (248 -579 nm) giving a total removal of 97 %. Adsorption was achieved in this incidence since the $TiO_2$ loading was three times (1.5 g/l) as much as that of the $TiO_2$ adsorption isotherms (0.5 g/l) discussed in section 4.5. In comparison the 2,4-D with the 10 % composite shows significant (93 %) adsorption in the dark but very little (<20 %) photodegradation occurred. At the initial 2,4-D concentration of 0.5 mM, the process is predominately adsorption.

The MCPA $TiO_2$ control results (Figure 4-32), show 62 % adsorption in the dark however less photodegradation (26 %) is shown at the same initial concentration compared to 2,4-D. This difference in photodegradation at the same concentration of the two analytes is most likely due to the fact that more adsorption occurred for MCPA and so there was less of this analyte available for photodegradation once the light was switched on. This difference in adsorption is most likely due to the difference in log P values between MCPA and 2,4-D.

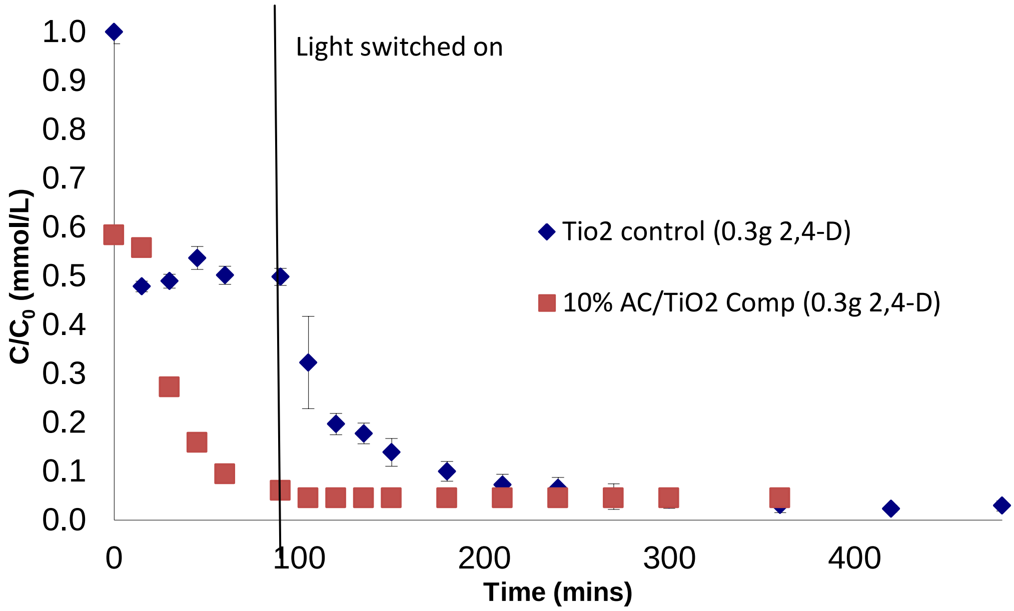


**Figure 4-31: $TiO_2$ control compared to 10 % $TiO_2$/AC for the removal of 2,4-D**

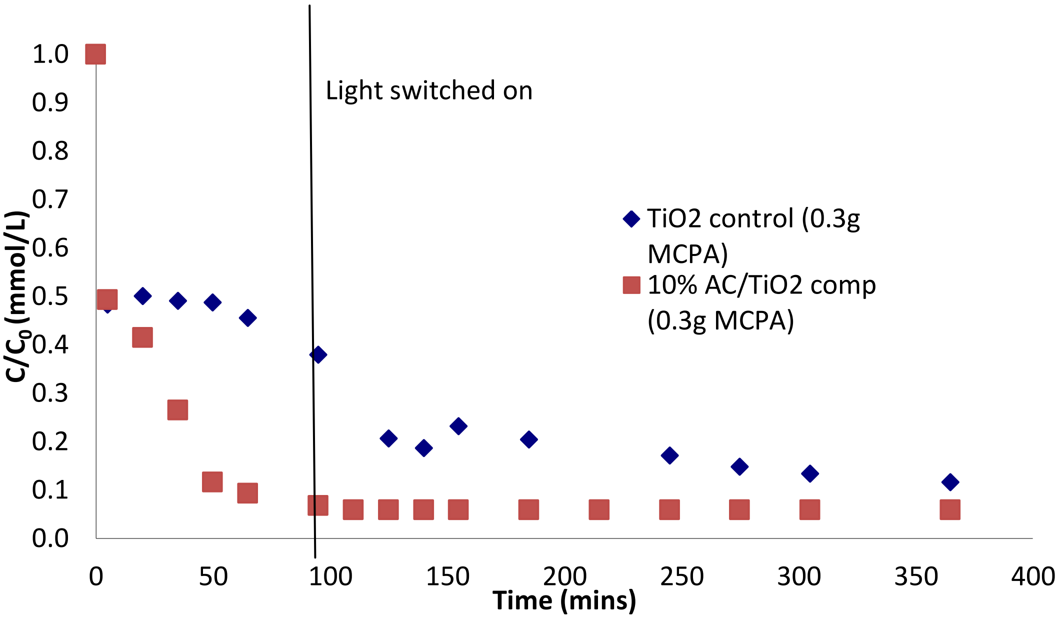


**Figure 4-32: $TiO_2$ control compared to 10 % $TiO_2$/AC for the removal of MCPA**

**pH effects of $TiO_2$ photocatalysis**

The effect of pH on the $TiO_2$ photocatalytic degradation of 2,4-D and MCPA has been previously investigated (Trillas, Peral and Domènech 1995, Djebbar, Zertal and Sehili 2006, Zertal, Sehili and Boule 2001). Figure 4-33 shows the photodegradation of 2,4-D using $TiO_2$ at pH 4, 5, 6, 10 and natural pH 3.3. These results compare to those in Figure 4-25 (pH study on 10 % $TiO_2$/AC) except no significant adsorption is noted when unmodified $TiO_2$ is used. The graph shows optimum degradation efficiencies at natural pH with 95 % removal. As the pH approaches pH 7 a reduction in removal efficiency is noted (15 % removal). A slight improvement in degradation efficiency is noted for pH 10 with 79 % removal. As discussed in chapter 2, there is a debate whether the pH of the initial concentration of the pesticide has an effect on the degradation of the 2,4-D when $TiO_2$ photocatalysis studies are performed. For 2,4-D removal it was stated that the degradation increases with increasing pH (pH6-12) by Djebbar *et al.*(1998) and that increasing pH decreases the $TiO_2$ activity (Herrmann and Guillard 2000). There is no consensus on whether or not high pH values influence the photodegradation of 2,4-D over $TiO_2$ but the results obtained here show that the natural pH is optimum for photodegradation and that at high alkaine pH such as pH 10, photodegradation occurs efficiently. There are two possibly reasons for this:

- As the pH of the solution increases above pH 4 the degradation capacity decreases as the compound becomes charged and therefore more water soluble.
- a change in Zeta potential with pH which will affect the adsorption properties of $TiO_2$ .

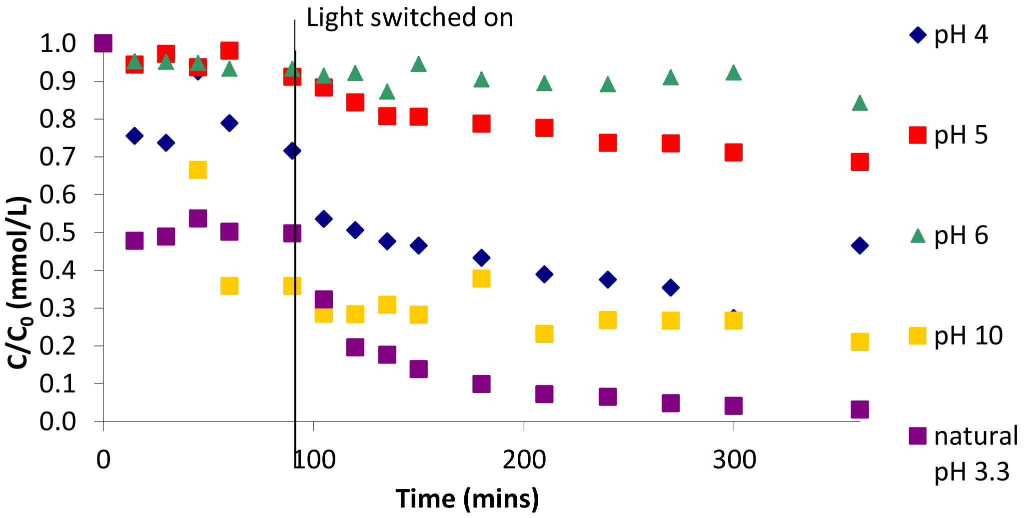


Figure 4-33: pH of 0.3g $TiO_2$ control for the photodegradation of 2,4-D

The total percentage removal of target analyte from test solution was calculated for each control experiment. The removal also was broken down into its adsorption and photodegradation components by calculating the percentage of analyte adsorbed in the dark and the percentage of analyte photodegraded in the presence of UV light. Table 4-4 and Table 4-5 show a summary of these data.

**Table 4-4: Adsorption, Photodegradation and Total Removal percentages of 2,4-D Controls**

| Control | Total Removal % | Adsorption % | Photodegradation % |
|---|---|---|---|
| Dark | 95 | 95 | - |
| Light | 97 | 78 | 19 |
| Activated Carbon | 95 | 77 | 18 |
| Titanium Dioxide Nat pH | 97 | 49 | 48 |
| Titanium Dioxide pH 4 | 54 | 16 | 38 |
| Titanium Dioxide pH 5 | 31 | 8 | 23 |
| Titanium Dioxide pH 6 | 15 | 11 | 4 |
| Titanium Dioxide pH 10 | 79 | 51 | 28 |

**Table 4-5: Adsorption, Photodegradation and Total Removal percentages of MCPA Controls**

| Control | Total Removal % | Adsorption % | Photodegradation % |
|---|---|---|---|
| Dark | 92 | 92 | - |
| Light | 98 | 95 | 3 |
| Activated Carbon | 97 | 89 | 8 |
| $TiO_2$ Nat PH | 88 | 55 | 33 |

### Controls comparison

The controls for each analyte were plotted against the optimum degradation conditions established from the optimisation section (Figure 4.34) and Figure 4-35). These graphs give a clearer overall picture of the adsorption and photodegradation components in the AC/$TiO_2$ system. The AC control, AC/$TiO_2$ and dark control showed similar results with 95 % removal rates. The $TiO_2$ control showed the poorest rate of overall degradation but showed the most efficient photodegradation for both 2,4-D and MCPA.

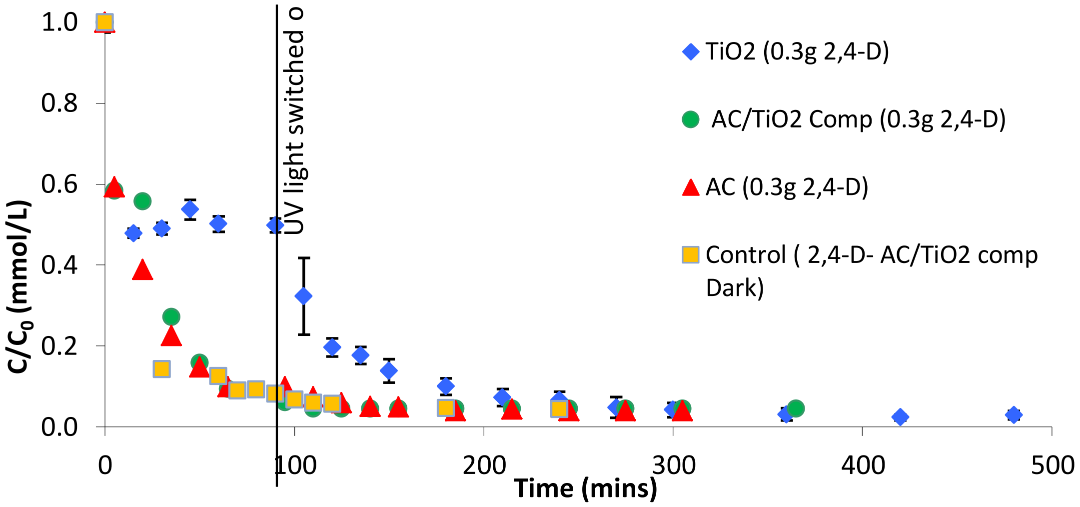


**Figure 4-34: Optimum conditions for the degradation of the 2,4-D (10 % comp 0.3g) compared to controls in the dark, activated carbon (Aquasorb) and titanium dioxide controls**

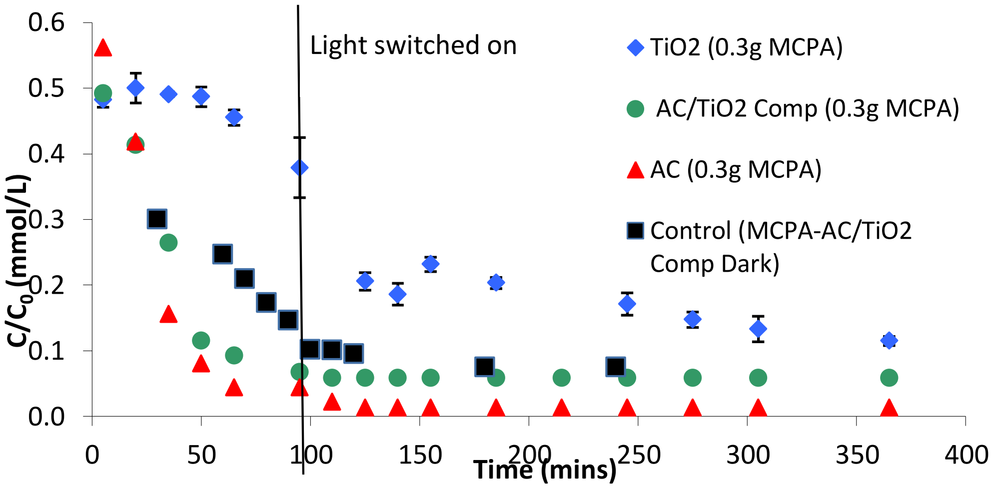


**Figure 4-35: Optimum conditions for the degradation of the MCPA (10 % comp 0.3g) compared to controls in the dark, activated carbon (Aquasorb) and titanium dioxide control**

## 4.6. AC/$TiO_2$ composite discussion and comparison to literature

There have been several research studies that considered the combination of $TiO_2$ and AC for the removal of a variety of pollutants (Lim *et al*. 2011, Cao *et al*. 2011, Jamil *et al.* 2012, Yap *et al.* 2012, Yap, Lim and Srinivasan 2011, Yap and Lim 2011). Methods of composite preparation differ between studies but the most common methods are chemical methods such as sol-gel and hydrothermal methods (Lim *et al*. 2011). In the current study a low temperature impregnation method of preparation was used as it was reported to be superior to high temperature preparation methods as the surface area of the $TiO_2$ particles is not decreased as a result of heat treatment (Keane *et al.* 2011, Ao *et al.* 2008). The major advantage of this method of preparation is the reduced chemical and energy consumption as well as the minimisation of environmental pollution when compared to methods such as high temperature calcination and sol-gel. However the disadvantage of this method is that the physical bonding of $TiO_2$ on the surface of AC is likely to be weak which may result in an appreciable amount of $TiO_2$ particles being dislodged from AC in solution (Lim *et al*. 2011).

To examine the physical, mineralogical and photochemical properties of the $TiO_2$/AC composite, there are a number of techniques employed, the most common methods being XRD, SEM, EDX, TEM and FTIR. For this study SEM and EDX were utilised. The composite surface morphology and elemental compositions were determined using these techniques it was shown that $TiO_2$ had deposited as particles onto AC. Images obtained compare well to those found in literature (Sun *et al*. 2009, Zhang, Zhou and Lei 2005).

As previously discussed in section 2.9 there is a limited amount of research on the removal of pesticides using AC/$TiO_2$ composites. Yoneyama *et al.* (2000) determined that 91.5 % of the initial concentration of Propyzamide was removed from aqueous solution after 300 mins when the $TiO_2$/AC composite (70 % $TiO_2$) was used compared to only 1.4 % removal when bare $TiO_2$ was used. The current study with target analytes 2,4-D and MCPA showed similar removal efficiencies of 97-98 % when the $TiO_2$/AC (10 % $TiO_2$) composite was used. Lower removal efficiencies for bare $TiO_2$ were determined (48 %) in the current study when compared to the study using Propyzamide where 100 % removal was noted.

Only one study that used one of the target analytes used in this thesis has been found in the literature. Matos *et al.* (2001) determined the removal of 2,4-D with $TiO_2$ and AC under photochemical conditions, with complete removal of the pesticide determined between 120-300 min. A composite was not used in this study, instead a suspension of AC and $TiO_2$ was utilised to remove 2,4-D. In the current study, as previously stated, 97-98 % removal was achieved for 2,4-D with the majority being removed via adsorption. Matos *et al.* found complete disappearance of 2,4-D and its intermediates by HPLC analyses. The lights sources used by Matos *et al.* (2001) were similar to those of the current study (125 W medium pressure lamp). The same $TiO_2$ was also used (P25 Degussa). However, there are a number of differences between the two studies, which could account for the difference in removal rates. Firstly, the Matos *et al.* (2001) study used two different activated carbons, a Merck activated carbon and an activated carbon called Purocarbon with BET surface areas of 775 $m^2/g$ and 1240 $m^2/g$ respectively, compared to the current study which used an activated carbon called Aquasorb 2000 on its own, with a BET surface area of 1050 $m^2/g$. Secondly, the Matos *et al.* (2001) used a suspension of 50mg of $TiO_2$ in water with 5 mg of AC in a 100 ml capacity reactor instead of a true composite. The current study used a 300 mg of composite or 300 mg of $TiO_2$ on its own (control) in a 200 ml reactor.

## 4.7 AC/$TiO_2$ composite conclusion

In order to utilise the AC/$TiO_2$ composite, studied in this thesis, for commercial water treatment there are a number of parameters which need further investigation;

1. Dispersibility and recovery from aqueous phase
2. UV light intensity
3. Stability of composite – mechanical and photo
4. Photocatalysis breakdown products

It is important that the composite is dispersed evenly throughout the analyte mixture. For this study the composite was dispersed mechanically by a magnetic stirrer. The design of the reactor, as shown in Figure 3-1, was not ideal for an even distribution of the composite. For commercial use a rotary type stirrer would be most suited to ensure an even distribution of the composite.

UV Intensity is another important issue. UV light needs to be distributed evenly throughout the photoreactor configuration in order to obtain efficient removal. The thesis study had an immersion well photoreactor placed in an aluminium lined cupboard so light distribution would be consistent. However, it has been suggested (Lim *et al.* 2011) that black AC may not be ideal as the $TiO_2$ support compared to other transparent and reflective substrates, since a black material absorbes a considerable amount of light. This effect may be a possible explanation as to why the $TiO_2$ photodegradation in the AC composite did not work as efficiently.

Stability is also an important issue. The stability of the composite to endure prolonged UV irradiation and the mechanical stability of the composite are the key issues. The composite needs to stay intact without displacement of $TiO_2$ from the AC surface. In this study some $TiO_2$ displacement was noted towards the end of the photochemical experiments. During some of the experiments it was observed that some $TiO_2$ came off the composite surface which could have affected the removal efficiency of the target analytes.

The chemical composition and structure of the target analyte is a very important factor to consider. Although removal of the target analytes 2,4-D and MCPA was not efficient, the same experimental setup has been used to successfully degrade pharmaceuticals such as famotodine (Keane *et al.* 2011), indomethacin and amoxicillin (Basha *et al.* 2011). The target analytes for the current study are chlorinated aromatics, which are highly stable to oxidation. This might explain the photocatalysis inefficiency observed with both target analytes. Famotidine, amoxicillin and indomethacin are not chlorinated and therefore easier to remove via photodegradation.

# 5 Results and Discussion for removal of pesticides 2,4-D and MCPA by dye/$TiO_2$ and dolomite/$TiO_2$ Composites

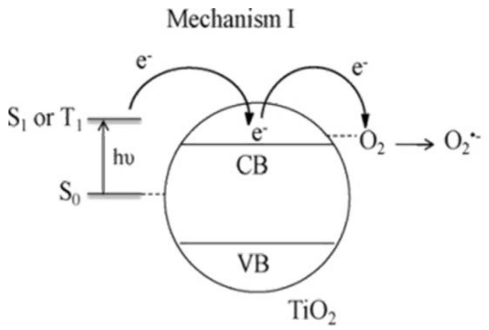
## 5.1. Dye/$TiO_2$ composites

### Introduction

There have been a number of studies on the use of dye sensitised $TiO_2$ composites for the removal of pollutants (Chatterjee and Mahata 2002, Chatterjee and Mahata 2004, Jiang *et al.* 2008, Li *et al.* 2008, Sun and Xu 2009, Lü *et al.* 2010, Mele *et al.* 2003). The majority of the research in this area has focused on the use of dye pigments for visible spectral sensitisation of $TiO_2$ to improve the efficiency in dye sensitised solar cells (Sun and Xu 2009). Although $TiO_2$ in the presence of UV radiation has become the benchmark photocatalyst for degradation of various pollutants in water (Chatterjee and Mahata 2004), its major drawback is that it absorbs only a small portion (5 % of light reaching Earth’s surface) of the solar spectrum in the UV region (band gap energy of 3.0-3.2 eV) and therefore is quite an expensive process (Sun and Xu 2009). The photosensitised degradation process has the advantage that it harvests maximum solar energy by utilizing visible light for degradation of water pollutants (Sun and Xu 2009).

There are many different dyes that can be used with $TiO_2$. These include methylene blue, rhodamine B (Chatterjee and Mahata 2002), phthalocyanines (Sun and Xu 2009) porphyrins (Lü *et al*. 2010, Mele *et al.* 2003, Wang *et al*. 2010b), thionine, eosin Y, nile blue A, safranine O (Chatterjee and Mahata 2004), chrysiodine G and tolyene-2,4-diisocyanate (Jiang *et al.* 2008). In the present study porphyrins and methylene blue were used to sensitise $TiO_2$ as they were readily available and had been used in previous studies within the research group (Murphy 2012, Murray 2012). Of the two dyes, most research has been conducted using porphyrins (Li et al. 2008, Lü *et al.* 2010, Mele *et al*. 2003, Wang *et al.* 2010b).

New composites were prepared combining $TiO_2$ and dyes. Three types of dye/$TiO_2$ composite were used; Porphyrin/$TiO_2$, Methylene Blue/$TiO_2$ and Brominated porphyrin/$TiO_2$. The advantage of a $TiO_2$/dye composite is that it should function in both the UV and visible regions of the solar spectrum. The proposed mechanism of action for dye/$TiO_2$ composites is outline in Figure 5-1. (Diaz-Uribe *et al.* 2010)



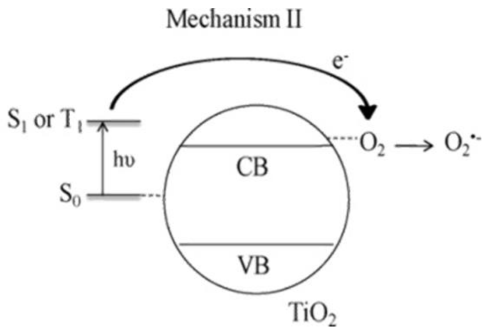


**Figure 5-1: Mechanism of superoxide anion generation. $S_0$ = sensitizer ground state, $S_1$ = singlet excited state, $T_1$ = triplet excited state, CB = conduction band, VB = valence band.**

Adsorption of UV-Vis radiation excites the sensitiser (dye) from a ground state to its singlet ($S_1$) state and triplet state ($T_1$). There are two proposed mechanisms for the fate of these excited states (Diaz-Uribe *et al.* 2010). The first mechanism (mechanism I) states that an electron is transferred from either the singlet or triplet excited state of the dye to the conduction band of $TiO_2$. If oxygen is adsorbed on the $TiO_2$ surface this oxygen can be reduced by the transferred electron from the conduction band yielding superoxide anion. The second postulated mechanism (mechanism II) states that an electron transfer occurs between the excited triplet state of the dye and oxygen generating the superoxide anion.

The dyes chosen for this application were 5,10,15,20-Tetrakis-(4-carboxyphenyl)-21,23H-porphyrin (TCPP) , methylene blue and 5,10,15,20-Tetrakis-(4-bromophenyl)-21,23H-porphyrin . Although these dyes absorb in the visible and UV regions of the solar spectrum, the visible region was selected for these studies as this would be more commercially advantageous. The new composites were prepared as outlined in section 5.1.2. All photodegradation experiments using the new composites included controls with unmodified $TiO_2$ and porphyrin/Methylene Blue to determine if the observed affects are a result of the composite or one of the individual components.

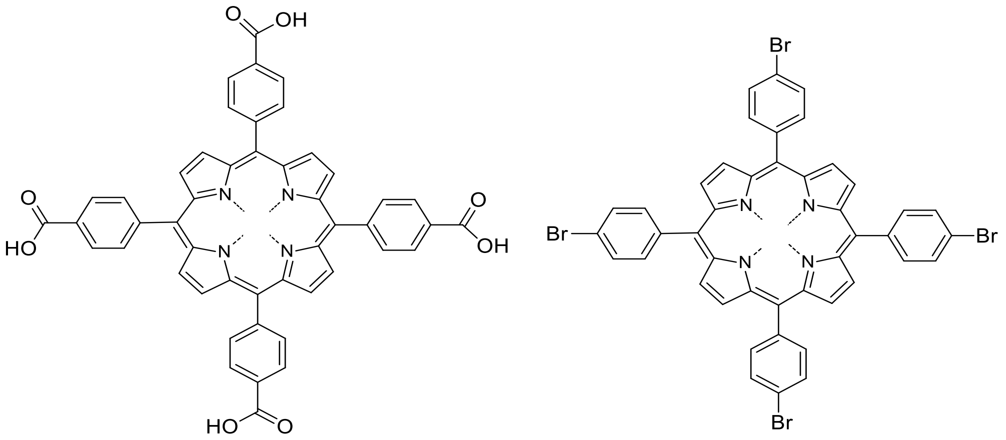


**Figure 5-2: Chemical structure of 5, 10, 15, 20 tetrakis-(4-carboxyphenyl)-21,23H-porphyrin (left) and brominated porphyrin (right).**

### 5.1.1. Preparation of Dye/$TiO_2$ composite

A previously developed method for the preparation for the porphyrin/$TiO_2$ composite developed by Murphy *et al.* (2012) was used. This method involved the dispersion of P25 into methanol by stirring followed by sonication for ten minutes. Once the $TiO_2$ was dispersed then 50 mg of TCPP was added and the mixture was stirred overnight. The product was then filtered and washed with methanol until the washings ran clear. After grinding with a mortar and pestle the product was a purple/brown colour.

For the methylene blue composite a low temperature impregnation method, using ultrasonication was developed for applying methylene blue to $TiO_2$. Deionised water (50 ml) was added to a 100 ml glass beaker. P25 (1 g) was added to the beaker along with methylene blue (0.0202 g). The solution was sonicated for an hour and then dried overnight at 110 $^0$C.

The brominated porphyrin composite was prepared using the same method of preparation as that TCPP composite.

### 5.1.2. Characterisation of dye/$TiO_2$ composite

In order to confirm the presence of the dyes on the composites, a series of spectral studies were undertaken. UV-Vis (Diffuse Reflectance) was performed on solid TCPP, TCPP-$TiO_2$ composite and $TiO_2$ (Figure 5-4). $TiO_2$ absorbs only in the UV region below 400nm whereas the composite and TCPP absorb in 400-700 nm region. Firstly the TCPP on its own in methanol was examined. The diffuse reflectance confirms the presense of prophyrin on the $TiO_2$ surface. A UV-Vis spectrum of the TCPP (Figure 5-3) shows the maximum adsorption (soret band) at 416nm and the Q bands at 512, 547, 589 and 643 nm.

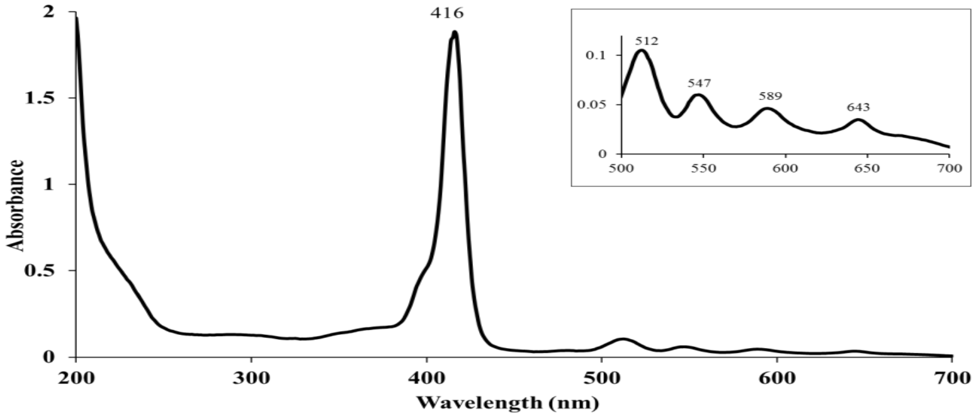


**Figure 5-3: UV-Vis spectra of TCPP in Methanol with Q bands (Murphy 2012)**

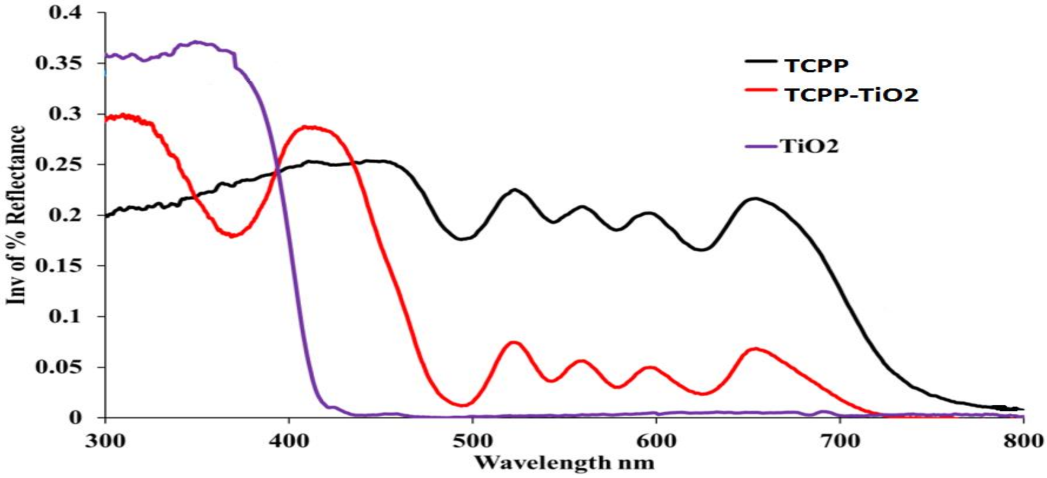


**Figure 5-4: Diffuse Reflectance UV-Vis Spectroscopy for TCPP-$TiO_2$, TCPP and $TiO_2$ (Murphy 2012)**

### 5.1.3. Photodegradation Results of porphyrin/$TiO_2$ composite

Photodegradation studies were performed on selected analytes using the dye composites. Initially famotidine was tested in the photodegradation experiments conducted using a halogen lamp emitting light between 380-740 nm (Figure 5-5). Famotidine was chosen as previous work had been conducted on this analyte and it had been shown that the Porphyrin/$TiO_2$ composite was efficient at removing this analyte (Murphy 2012). The porphyrin used was TCPP (Figure 5-5).

Rapid photodegradation was noted with the HPLC famotidine peaks disappearing in the chromatogram after 100 min (Figure 5.5). Controls of unmodified $TiO_2$ and porphyrin at the same concentration as the TCPP/$TiO_2$ were also examined under visible light and it was determined that separately the components did not degrade famotidine. Thus, the observed photodegradation is indeed a composite effect.

The same experimental setup was then used for the photodegradation of the herbicides. The results of these experiments are shown in Figure 5-6. The TCPP/$TiO_2$ composite was not found to be an effective composite for the photodegradation of the herbicides ( Figure 5-6) under visible light. The same initial concentration of 28 ppm was used. No discernible degradation was noted. This shows that this particular composite does not work on MCPA and 2,4-D but can work effectively with certain pharmaceuticals.

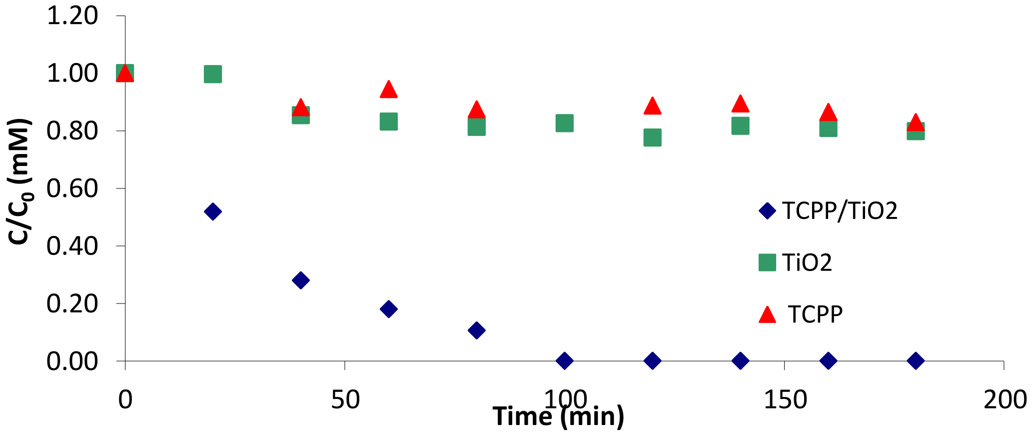


**Figure 5-5: Photodegradation of famotidine with TCPP/$TiO_2$ composite also porphyrin (TCPP) and $TiO_2$ control under visible light.**

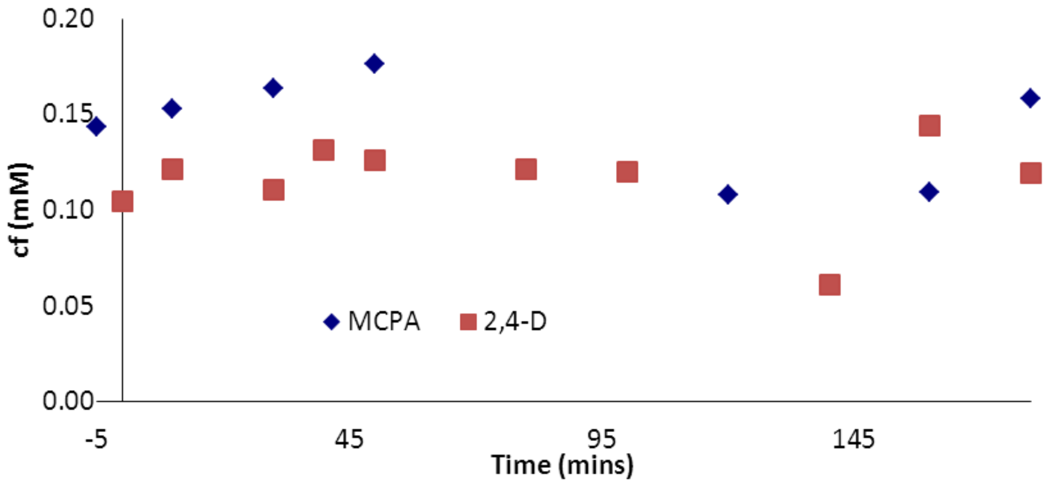


**Figure 5-6: Photodegradation of 2,4-D and MCPA with TCPP/$TiO_2$ composite under visible light**

### 5.1.4. Photodegradation Results of Composite brominated porphyrin/$TiO_2$ composite and methylene blue/$TiO_2$ composite

The brominated porphyrin/$TiO_2$ composite (Figure 5.2) was also investigated for the removal of famotidine under visible light (Figure 5-7). It was determined that no discernible degradation was achieved, However, it was also observed that the composite did not ‘stay intact’ throughout the experiment, it was evident that porphyrin was dissolving off of the $TiO_2$ surface into solution, a phenomena that was not observed with the TCPP/$TiO_2$ composite.

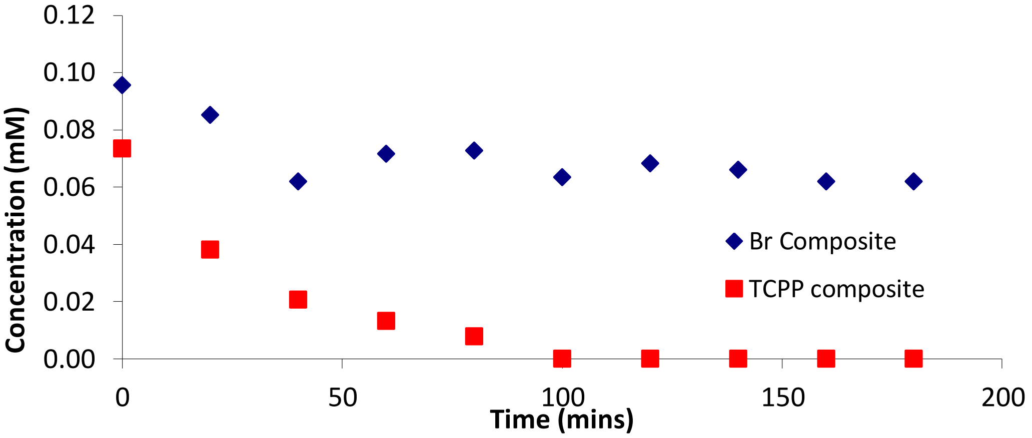


**Figure 5-7: Photodegradation of famotidine with brominated porphyrin/$TiO_2$ composite compared to non-brominated porphyrin/$TiO_2$ composite.**

Methylene blue was also investigated as an alternative photosensitiser for $TiO_{2.}$ The experimental conditions remained the same as for the TCPP/$TiO_2$. The results (Figure 5-8) show no significant photodegradation for 2,4-D.

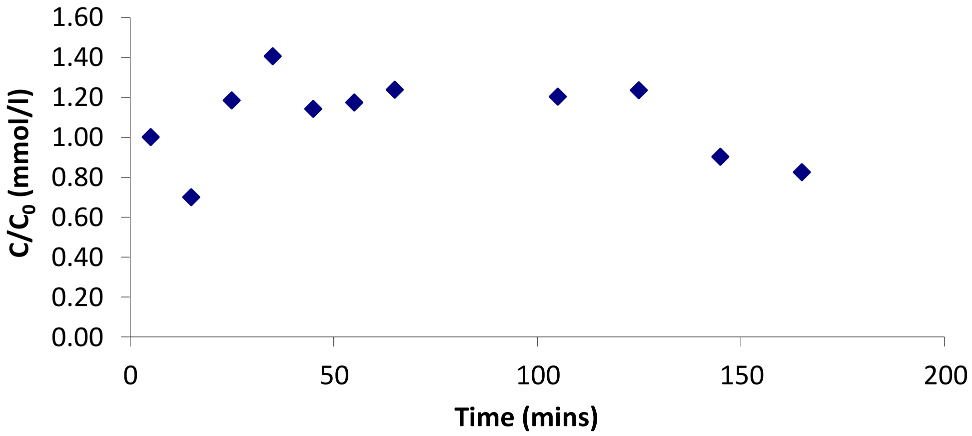


**Figure 5-8: Photodegradation of 2,4-D with Methylene Blue/$TiO_2$ composite under visible light**

An experiment was carried out where the TCPP/$TiO_2$ composite was used to remove methylene blue from solution under visible light conditions (methylene blue as the analyte). Methylene blue was indeed efficiently removed; however, upon physical analysis of the recovered TCPP/$TiO_2$ composite it was evident that methylene blue coated the surface of the composite (was strong blue in colour). To confirm that adsorption was the main removal mechanism, control experiments were carried out with TCPP/$TiO_2$ methylene blue in the dark, and methylene blue was removed from solution by adsorption.

This result is significant since previous workers have reported the successful removal of methylene blue with dye/$TiO_2$ composites with photocatalysis (Jiang *et al*. 2008), however the work presented here (and reproduced by Murray 2012) indicates that methylene blue strongly adsorbs to the dye/$TiO_2$ composite and does not photodegrade.

Another important conclusion from this work is that dyes possessing carboxylic acid groups seem to bond efficiently to the $TiO_2$ surface (perhaps only a monolayer is formed) and are photoactive. However, the other two dyes that were used do not seem to 'bond to the surface efficiently (bromoporphyrin) or they seem to form thicker coats on the surface which quenches the potential photoactivity of the system. A plausible explanation for this is that $TiO_2$ is a 'basic' compound therefore it should be possible for the basic $TiO_2$ surface to react with the acid groups of TCPP to form stable ionic bonds.

### 5.1.5. Dye/$TiO_2$ composite conclusion

The methods of dye $TiO_2$ composite synthesis vary between studies but most mix the $TiO_2$ and dye together in a solvent with heat and filter and wash the resulting composite. In the present study as described in section 5.1.2, the porphyrin dyes and methylene blue were mixed with $TiO_2$ in methanol, magnetically stirred overnight at room temperature and then filtered and washed. It should be noted that this method was compared to a previous study ((Li *et al.* 2008)) which used harsher conditions (using strong solvents) and it was found that identical products were formed with both methods. It was decided to use the less harsh method.

The methods available for characterisation of the dye/$TiO_2$ composite are quite diverse. The most common techniques include UV-vis absorption (Chatterjee and Mahata 2002, Jiang *et al*. 2008, Jiang *et al*. 2008, Li *et al*. 2008, Sun and Xu 2009, Lü *et al.* 2010). X-ray diffraction (XRD) (Jiang *et al*. 2008, Jiang *et al*. 2008, Lü *et al.* 2010, Mele *et al*. 2003) and diffuse reflectance spectroscopy (DRS) (Jiang et al. 2008, Sun and Xu 2009, Mele *et al.* 2003, Wang *et al*. 2010b). The current study used both UV-vis and UV-vis DRS. No study could be found that uses the same porphyrin that is used in the present study but similar porphyrins were found (Jiang et *al*. 2008, Mele *et al*. 2003).

One of the most important parameters to look for in dye/$TiO_2$ studies is the pollutant photodegradation performance. As with the AC/$TiO_2$ composite most of the studies centre around the use of organic dyes or simple phenolic compounds as target pollutants, none of which are comparable to the current study (Murphy *et al.* 2012). Murphy *et al.* (2012) tested three pharmaceuticals as target pollutants: famotidine, tamsulosin and solifenacin under both solar light and 500 W visible lamp. The composite was found to partially oxidise famotidine to a sulfoxide but did not completely mineralise it. The composite did not work effectively for the removal of tamsulosin or solifenacin. The composite was found to have selective oxidation for famotidine. This photosensitised dye/$TiO_2$ process breaks down pollutants via the generation of superoxide anions ($^{\cdot}O_2^{-}$) as explained in 5.1.1. However these superoxide anions have a lower redox potential than the hydroxyl radicals ($^{\cdot}OH^{-}$) generated in the AC/$TiO_2$ composite removal process. The target pesticides 2,4-D and MCPA are chlorinated aromatics which require a high redox potential to be broken down and thus appear to be unaffected by superoxide anion. This explains why the TCPP/$TiO_2$ composite that was used in the present study was unable to breakdown the target analytes.

The only study that could be located on the use of dye sensitised $TiO_2$ for the removal of pesticides looked at the removal of Atrazine using the dyes thionine and eosin Y (Chatterjee and Mahata 2004). It was determined that eosin Y/$TiO_2$ composite gave 62 % removal of Atrazine from solution whereas the thionine/$TiO_2$ composite gave 54 % removal of Atrazine. This study only used a UV-vis spectrophotometer for analyte detection whereas Murphy *et al*. (2012) used both HPLC and LC-MS detection for more accurate analysis of degradation. Either this area has not been studied sufficiently for the removal of pesticides or like the current study, pesticides are too recalcitrant for this composite removal technique.

From the available studies on dye/$TiO_2$ composites it is important to note that aeration played a significant part in the removal of target pollutants. Sun *et al.* 2009 conducted the photocatalysis reaction by bubbling pure $O_2$, pure $N_2$, and pure $N_2$ with $AgNO_3$ through the aqueous suspension. It was determined that bubbling the reaction with pure $O_2$ gave the best removal. The authors' hypothesis was that the electron scavenger $O_2$ prevents the dye radicals from recombining with electrons on $TiO_2$ which results in improved degradation. In hindsight, perhaps $O_2$ bubbling could have aided the photodegradation of the target analytes in the current study.

## 5.2. Dolomite/$TiO_2$ composite

### 5.2.1. Introduction

As discussed in chapter 4, adsorption appears to be the dominating process in the removal of the target analytes using the AC/$TiO_2$ composite. One possible reason for this could be the fact that AC is a black compound and therefore absorbs all light equally on its surface, making it very difficult for light to penetrate through the pores to activate the $TiO_2$ present in the AC/$TiO_2$ composite. $TiO_2$ photocatalysis may be less efficient (section 4.5) when combined with AC. Therefore, it was decided to investigate a white compound to compliment the $TiO_2$ in a composite. Dolomite was chosen for this purpose.

Dolomite is a common sedimentary rock-forming mineral that can be found in sedimentary beds several hundred feet thick. It is also found in metamorphic marbles, hydrothermal veins and replacement deposits. It is abundant in Northern Ireland. The general formula of this mineral is $AB(CO_3)_2$, where A can be calcium, barium and/or strontium and the B can be iron, magnesium, zinc and/or manganese (Walker *et al.* 2003). For the purpose of this study dolomite with a chemical composition of $CaMg(CO_3)_2$ will be used as an adsorbent and will also be combined with $TiO_2$ to form a new photoactive composite which will be screened against 2,4-D and MCPA. The dolomite used in this study was calcined prior to use.

### 5.2.2. Preparation of Dolomite/$TiO_2$ Composite

The dolomite/$TiO_2$ composite was prepared using two different methods. The first was a low temperature impregnation method as outlined in the preparation of the AC/$TiO_2$ composite (section 4.2) except dolomite was used instead of AC.

The second method of preparation was a sol-gel method (Gholamvand 2013) where 200 ml of isopropanol alcohol was mixed with 20 ml of TTIP, (titanium isopropoxide). 10 ml of nitric acid was then added drop wise to this solution along with 600 ml of water. The solution was stirred overnight and the pH adjusted to pH 7 by $NH_4OH$ addition.

3 g of the prepared $TiO_2$ was stirred in 300 ml of deionised water, the resulting solution was then sonicated for 1 hour and then mixed with 15 g of dolomite. The solution was then dried at 80 $^oC$ overnight and calcined at 450 $^oC$ for 2 hr.

### 5.2.3. Characterisation of Dolomite/$TiO_2$ Composite

The dolomite/$TiO_2$ composite was characterized by SEM and XRD. Dolomite on its own was imaged first Figure 5-9 and Figure 5-10. The images showed individual grains of dolomite powder. The pores are not as visible in dolomite as those that are present in the images of AC (section 4.3, Figure 4-1 ).

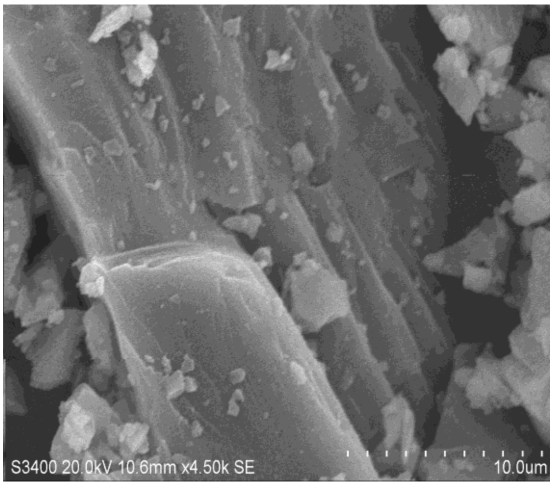


**Figure 5-9: Bare dolomite imaged at 4.5k magnification**

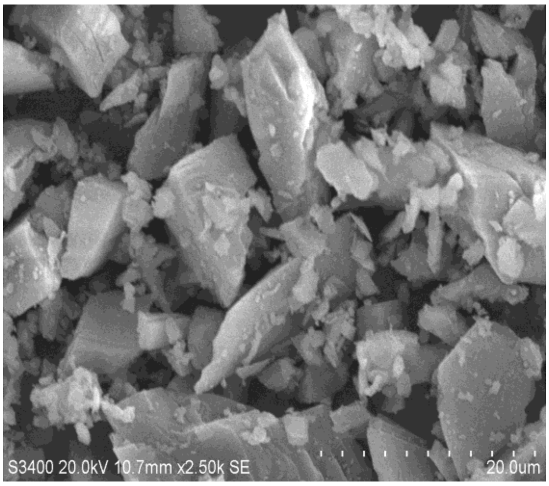


**Figure 5-10: Bare dolomite imaged at 2.5k magnification**

Images of the composite were also taken (Figure 5-11 and Figure 5-12). Here $TiO_2$ can be seen on the surface of the dolomite powder.

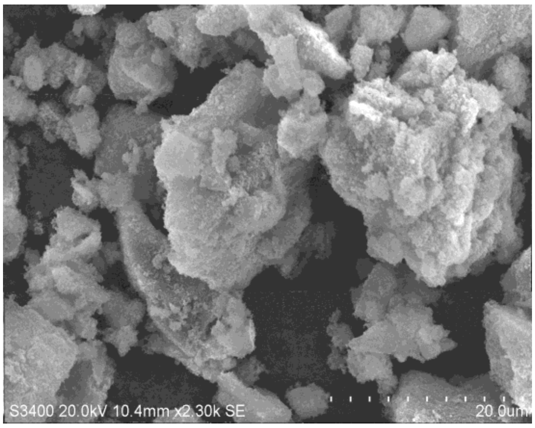


**Figure 5-11: Composite sol-gel imaged at 2. 3k magnification**

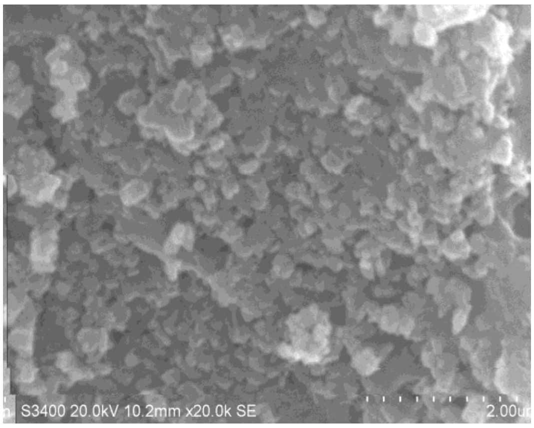


**Figure 5-12: Composite sol-gel imaged at 20k magnification**

X-Ray Diffraction (XRD) was also performed on the dolomite/$TiO_2$ composite and a summary of the results are shown below in Figure 5-13. The anatase phase of the $TiO_2$ can be clearly seen at 25 degrees in all the samples except the $TiO_2$Sol that was calcined (SOLCA). The dolomite/$TiO_2$ composite is shown as both DST8CA and DPT8NCA. The difference between these is that DST8CA was made using the Sol-gel method and the other was made with P25 $TiO_{2.}$ X-Ray Diffraction of bare dolomite is shown in Figure 5-14 as a comparison.

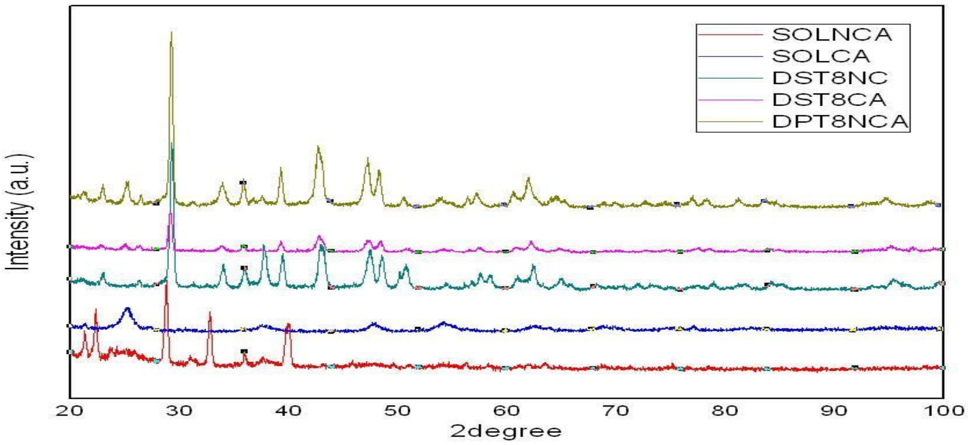


**Figure 5-13:X-Ray Diffraction of dolomite/ $TiO_2$ composite. SOLNCA= $TiO_2$ Sol dried without calcination, SOLCA= $TiO_2$ Sol dried at 450$^0$C for 2hr, DST8NC=Dolomite coated with $TiO_2$ Sol non calcined, DST8CA= Dolomite/$TiO_2$ Sol dried at 450$^0$C for 2hr and DPT8NCA= Dolomite/P25 non calcined (Gholamvand 2012)**

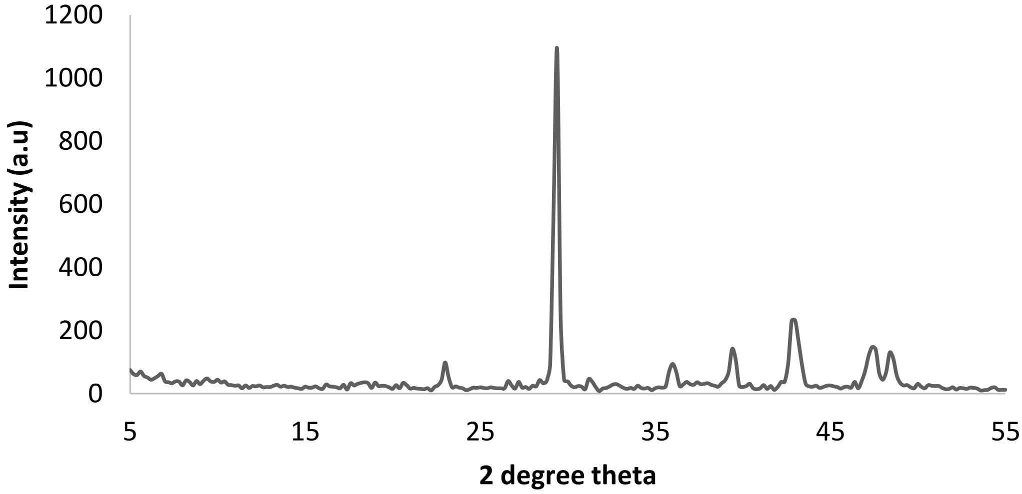


**Figure 5-14 : X-Ray diffraction of bare Dolomite (Gholamvand 2012)**

### 5.2.4. Results of Dolomite/$TiO_2$ composite

The adsorption of the dolomite was investigated first to establish a comparison between it and AC. Adsorption isotherms were performed in a similar way to those outlined in section 3.2.2. Results of these isotherms (Figure 5-15) show a significant difference in adsorption capacity between AC and dolomite. AC adsorbs MCPA with a higher q loading value and lower final concentration (meaning less of the analyte is left in solution) than dolomite. The most efficient percentage adsorption of MCPA with dolomite was observed at an initial concentration of 0.2 mmol/L with 22 % adsorption. At this corresponding initial concentration AC gave 95 % adsorption of MCPA. Therefore dolomite is not as effective an adsorbent as AC. Despite this, dolomite had been used as an adsorbent to remove a number of metals such as Lead(II) (Lee *et al.* 2006a) Copper(II) (Pehlivan *et al.* 2009), Arsenate(Ayoub and Mehawej 2007), Strontium (II) and Barium (II) (Ghaemi, Torab-Mostaedi and Ghannadi-Maragheh 2011).

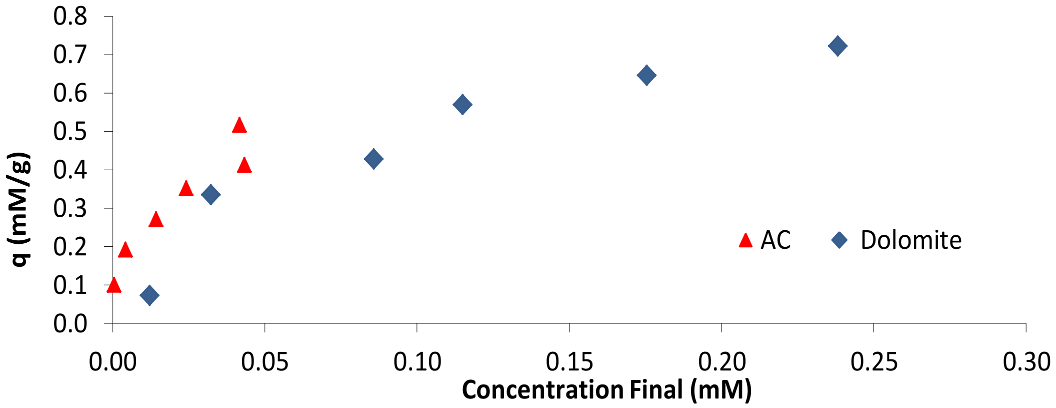


**Figure 5-15: Adsorption isotherm of MCPA onto AC and dolomite**

Photodegradation experiments were then performed with 2,4-D as outlined in section 3.2.3 using the two dolomite composites and UV light. Results for both composites are shown in Figure 5-16. It was noted that no discernible difference was observed in terms of photodegradation for each of the two composites, neither of the composites produced significant photodegradation of the target analyte.

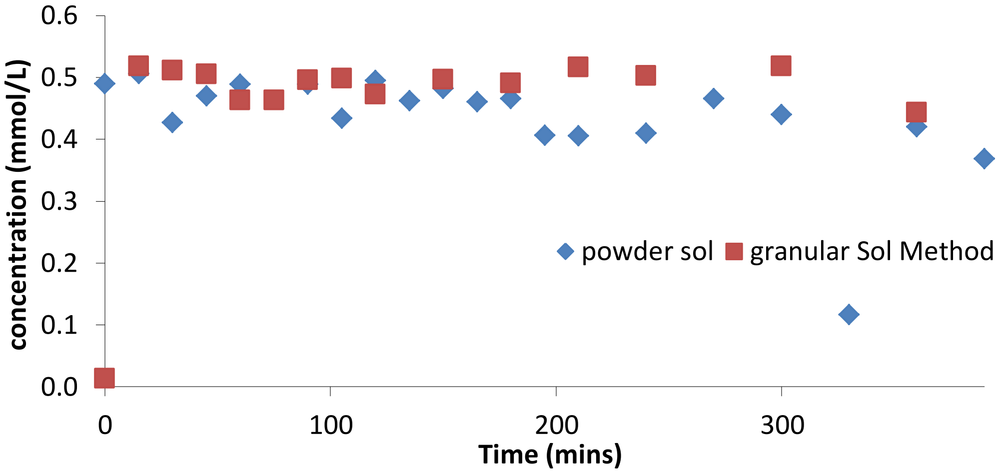


**Figure 5-16: Photodegradation of 2,4-D with the dolomite/$TiO_2$ composite- two methods of preparation**

It should be noted that the initial composite was composed of powdered dolomite sourced from Queen's University Northern Ireland. The particle size of this dolomite was comparable to the particle size of $TiO_2$ (nanoparticle size range), in all previous composite studies using AC, the AC is far larger in size than $TiO_2$. To determine if dolomite particle size was an issue in composite performance granular dolomite, of the same chemical composition, was sourced and used in place of the finely powdered dolomite. Results of the photodegradation of 2,4-D using both the granular and powdered dolomite are shown in Figure 5-17. No apparent difference was noted in terms of photocatalytic efficiency.

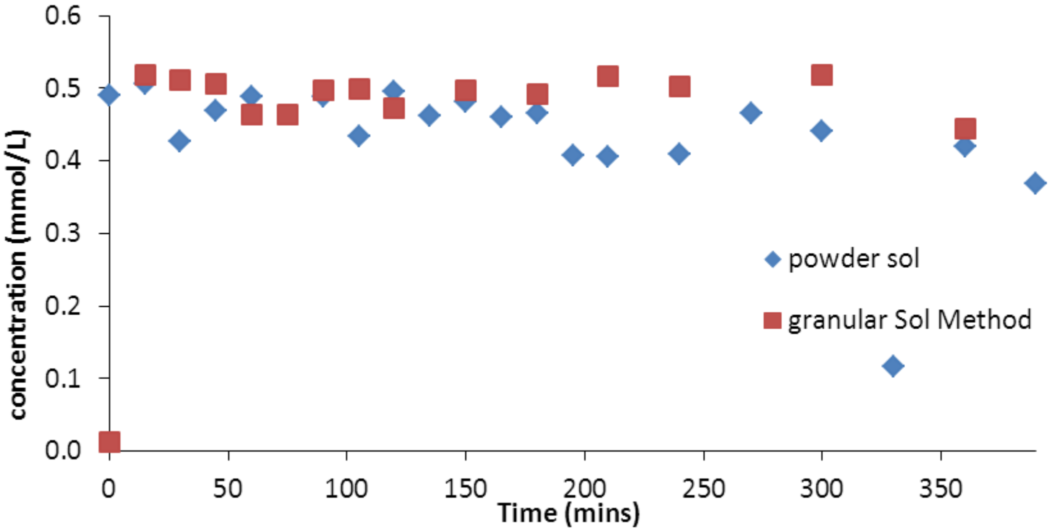


**Figure 5-17: Photodegradation of 2,4-D with dolomite/$TiO_2$ composite – powder and granular dolomite**

A control experiment was also run using just $TiO_2$ with 2,4-D under UV irradiation and the results are shown in Figure 5-18. It is evident that $TiO_2$ is removing 2,4-D. However, when the dolomite/$TiO_2$ composite photodegradation results are compared with the $TiO_2$ control it can be seen that the dolomite in the composite would appear to be quenching the photocatalytic properties of the $TiO_2$. $TiO_2$ photocatalysis quenching is not commonly reported however there have been some studies in this area. One such study (Di Vece *et al.* 2012) found that the presence of silver nanoparticles in $TiO_2$ porous layers, have an adverse effect on the photocatalytic degradation of ethylene. However, another effect is being observed with this new composite.

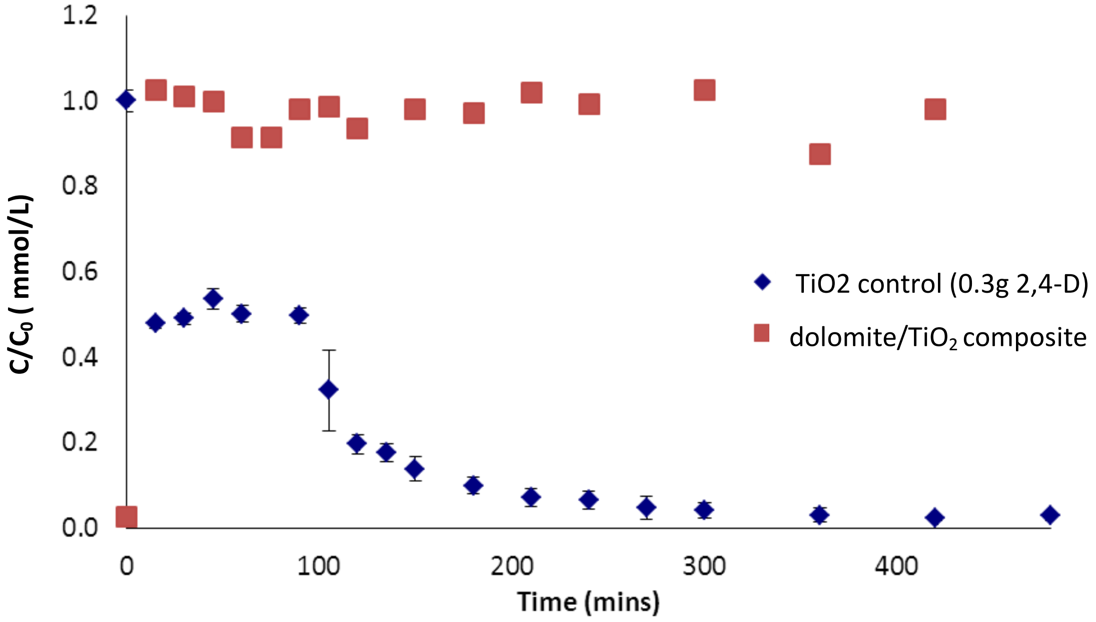


**Figure 5-18: 2,4-D photodegradation with dolomite/TiO$_2$ composite and TiO$_2$ control**

The current study however can be compared to a colleague's study within our group (Gholamvand 2013). The pharmaceutical famotidine was also investigated under photocatalytic conditions using a dolomite/TiO$_2$ composite (Figure 5-19).

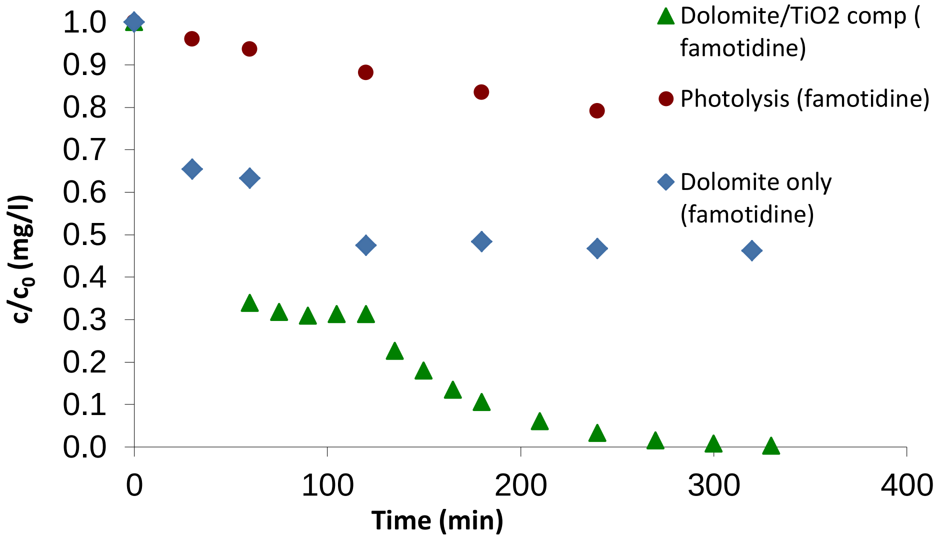


**Figure 5-19: Dolomite/TiO$_2$ composite for the removal of famotidine (Gholamvand 2013)**

Over 99 % removal of famotidine was achieved when the dolomite/$TiO_2$ composite was used, 88 % was removed using the dolomite only and 21% was removed by photolysis. These results confirm that the dolomite/$TiO_2$ composite is indeed photoactive, therefore in the case of 2,4-D another mechanism which is inhibiting photolysis must be occurring.

It was expected that the dolomite/$TiO_2$ composite would work more effectively at removing the target pollutants than $TiO_2$/AC. Dolomite, unlike AC, is a white compound thus light penetration should be more efficient for the dolomite/$TiO_2$ composite compared to the AC/$TiO_2$ composite. However this was not found to be the case with the dolomite/$TiO_2$ composite with 2,4-D (Figure 5-18).

There are no studies in the literature that utilise dolomite/$TiO_2$ composites to photodegrade any organic compounds to the best of the author's knowledge. To better understand the failure of the dolomite/$TiO_2$ composite further control studies were carried out using $TiO_2$ photocatalysis alone.

# 6 $TiO_2$ Photocatalysis – further results

## 6.1. Introduction

$TiO_2$ photocatalysis utilising UV-light and visible light (dye/$TiO_2$ composite only) is the backbone of the entire study as it forms the basis of all three composites. In section 4.5 when $TiO_2$ controls were investigated it was determined that $TiO_2$ photocatalysis of 2,4-D achieved a removal of 97 %. However when this was examined further only 47 % was actually photodegraded the remainder (50 %) was removed via adsorption. For MCPA $TiO_2$ controls there was an overall removal of 88 % (62 % adsorption and 26 % photodegradation).

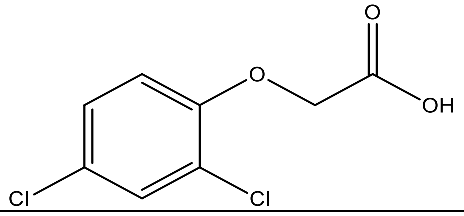
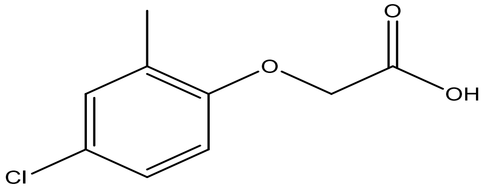
$TiO_2$ photocatalysis will be discussed in more detail in this chapter in order to investigate the degradation pathway of the target pesticides and to better understand the failure of the dolomite/$TiO_2$ composite under UV conditions. To achieve this end $TiO_2$ photocatalysis will be examined further by looking at the mass spectra of 2,4-D and MCPA samples that have undergone $TiO_2$ photocatalysis and the effect of the addition of hydrogen peroxide to the photocatalysis system will also be investigated.

## 6.2. Mass Spectrometry Data for $TiO_2$ UV photocatalysis

As previously mentioned an apparent reduction in the target HPLC analyte peak 2,4-D and the appearance of an unknown peak initially suggested that photodegradation was occurring with $TiO_2$ UV photocatalysis controls (section 4.5.2). In order to better understand the degradation pathway of 2,4-D and MCPA under $TiO_2$ photocatalysis, mass spectrometry was utilised. To optimise the mass spectrometry method, standards of the target analytes were run with a concentration of 5 ppm as this was the concentration that gave the highest signal.

Parent and daughter ions for both analytes were established (Table 6-1) a proposed fragmentation of 2,4-D by MS-MS is shown in Figure 6-2 where the daughter ions with m/z of 161 and 175 are produced. Samples from the reaction mixtures were then taken at time intervals of 60, 100 and 240 min. When these samples were analysed by HPLC, a second peak immediately appeared in the chromatogram (Figure 6-1). .

**Table 6-1: Table showing structures, parent and daughter ions for a 5ppm standard of both 2,4-D and MCPA**

| **Analyte** | **Structure** | **Mass m/z** | **Daughter ions m/z** | **Mol. Wt. g/mol** |
|---|---|---|---|---|
| 2,4-D |  | 218.9 | 161 | 221.04 |
| MCPA |  | 199 | 141,155 | 200.62 |

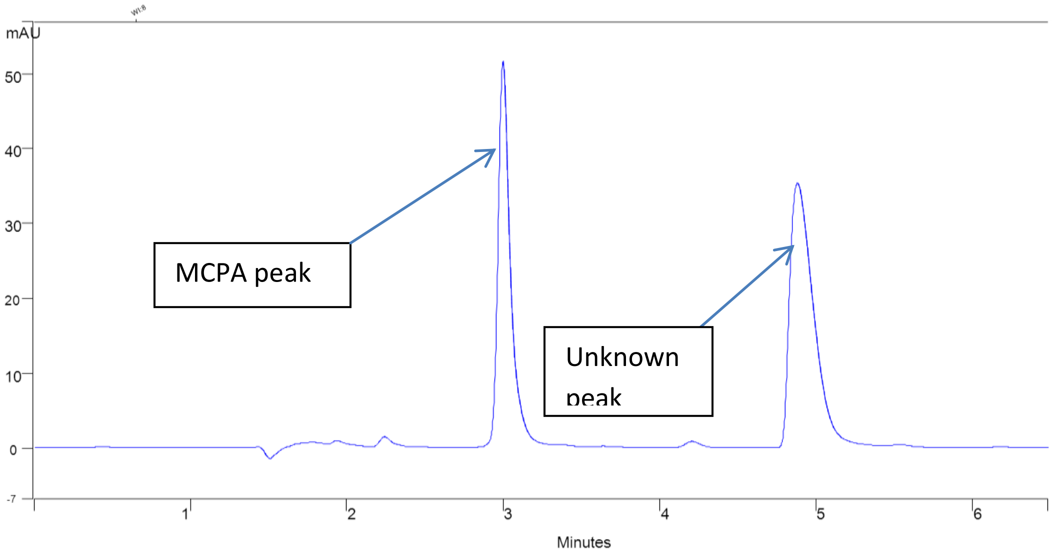


**Figure 6-1 : Sample chromatogram showing MCPA and unknown peak**

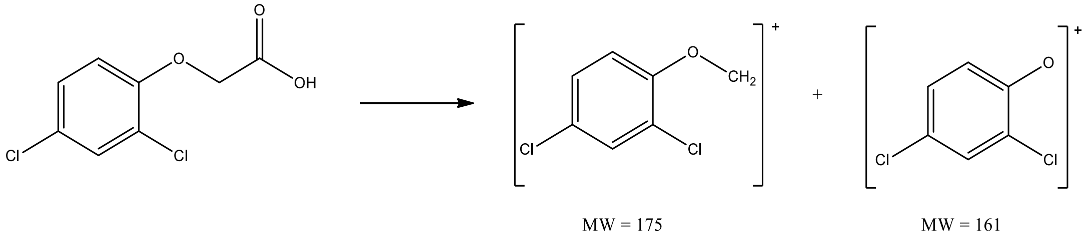


**Figure 6-2: Proposed fragmentation for 2,4-D using MS-MS**

Direct injection of these samples showed the presence of two peaks with a mass to charge ratio of 218.9 and 162.9 as show in Figure 6-3. For comparison a 0.025mmol/L standard peak of 2,4-D is shown in Figure 6-4. The difference in mass between the 162.9 and 218.9 peaks is 60 which would indicate the loss of acetic acid from the compound. In order to confirm this an experiment was run with a standard of 2,4-D spiked with 2,4-dichlorophenol (the proposed degradant). HPLC results indicate that 2,4-dichlorophenol is not present in high concentrations (the intensity of the mass spectral peaks is not an indication of relative concentrations but of ion stability) and that the observed peak in the chromatogram at 5.8 minutes is not due to a degradant; however it was identified as the free acid form of 2,4-D. It should also be noted that a peak also appeared at this retention time in some previous chromatograms of 2,4-D standards that were left standing, which showed that the possible intermediate was not 2,4-D-dichlorophenol but instead the acid form of 2,4-D (Figure 6-5). Therefore, $TiO_2$ photocatalysis does not completely photodegrade 2,4-D and the same can be said for MCPA (Figure 6-6 and Figure 6-7). Further MS Data can be seen in the appendices.

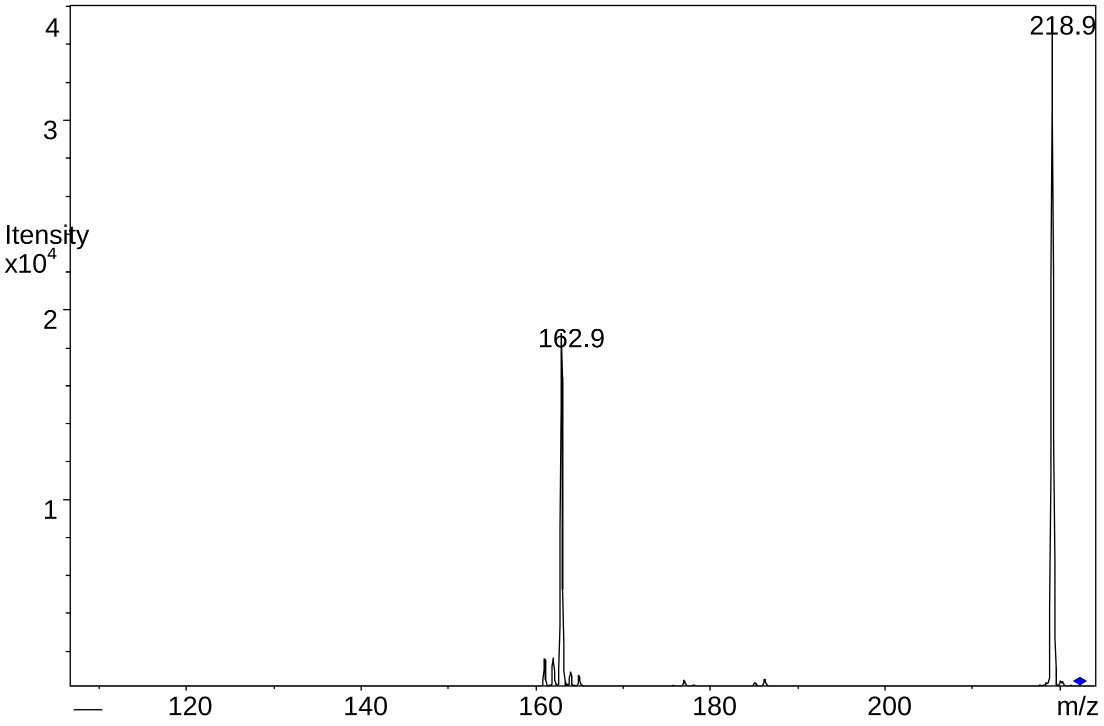


**Figure 6-3: 2,4-D $TiO_2$ photocatalysis (100 min) showing the analyte peak at mass 218.9 and the intermediate peak at mass 162.9 (ESI Negative mode)**

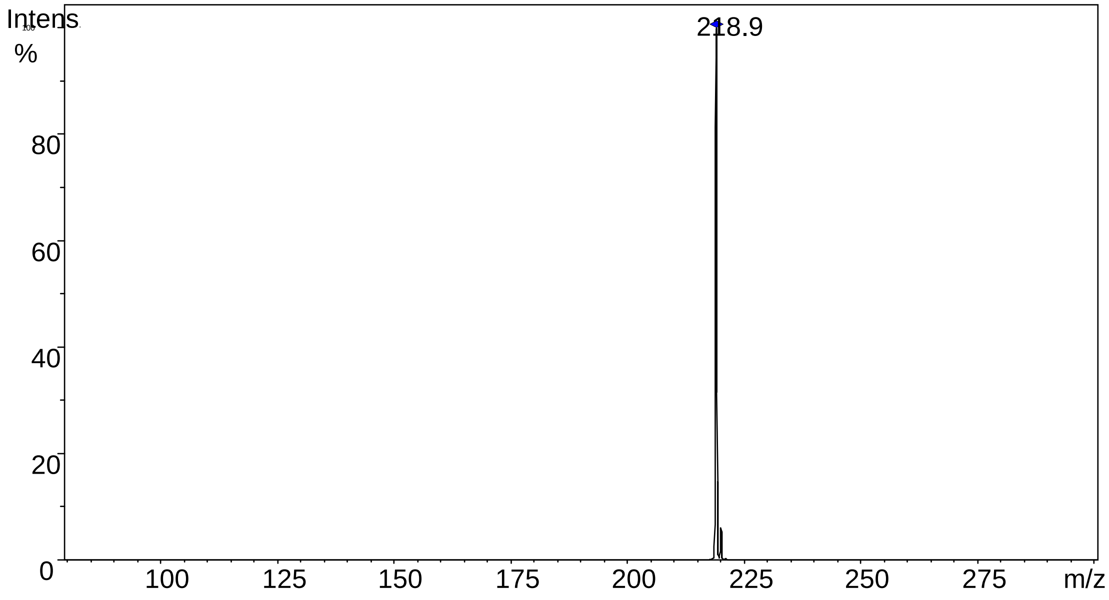


**Figure 6-4: 2,4-D 5 ppm (0.025 mmol/L) standard directly infused to MS (ESI negative mode)**

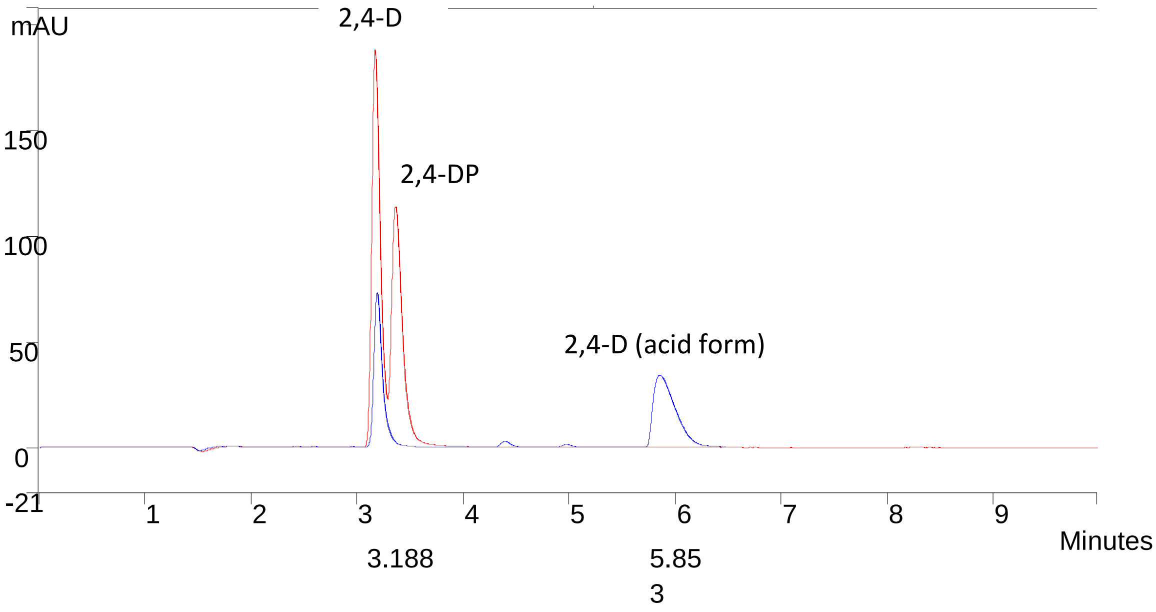


**Figure 6-5: LC chromatogram showing $TiO_2$ photocatalysis of 2,4-D after 60 min of irradiation (blue) and standard mix of 100ppm 2,4-D and 100ppm 2,4-DP (red)**

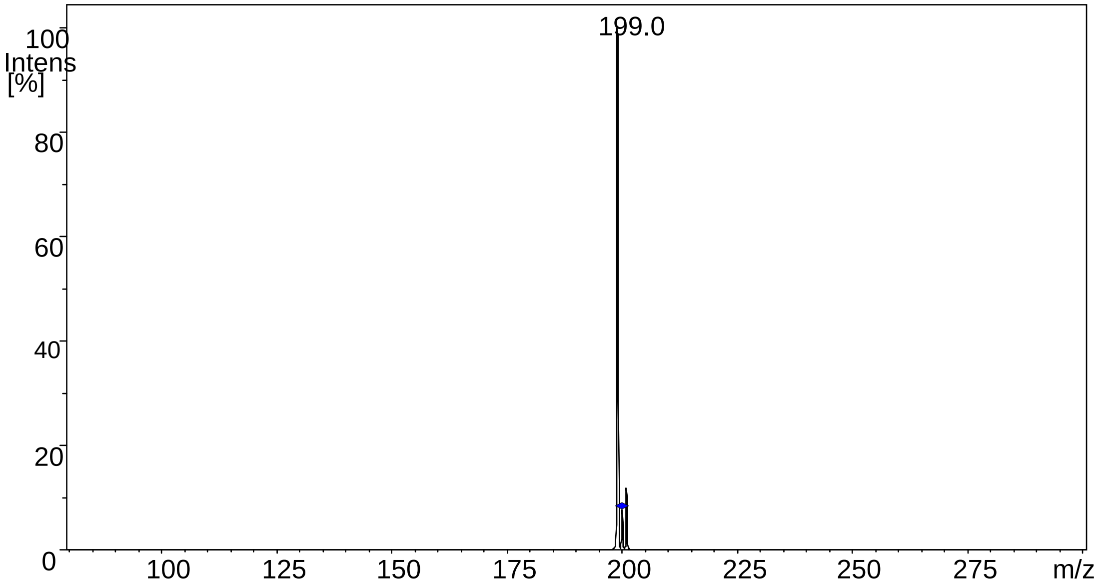


**Figure 6-6: MCPA 5 ppm (0.025 mmol/L) standard directly infused to MS (ESI negative mode)**

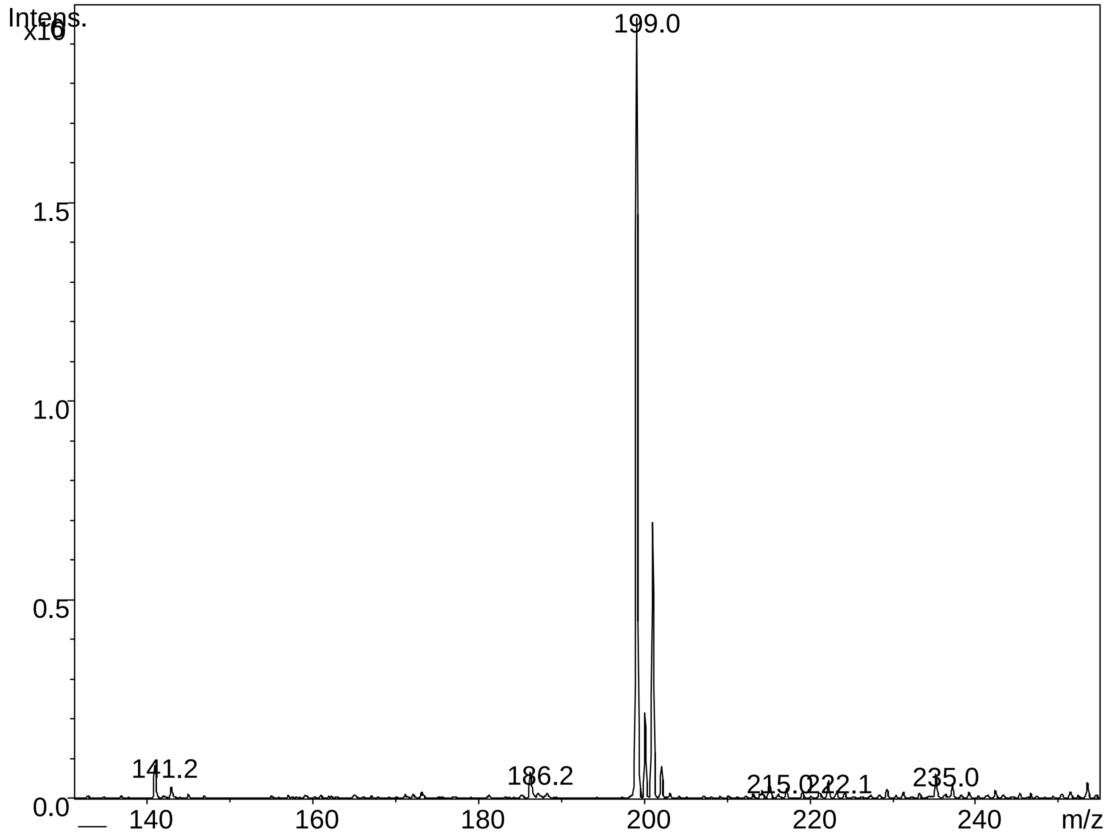


**Figure 6-7: Mass Spectra of MCPA $TiO_2$ photocatalysis (60 min) showing the parent ion at 199 (ESI negative mode)**

There are a number of studies which claim to have achieved complete degradation of the target analytes using $TiO_2$ photocatalysis. One of these studies (Djebbar, Zertal and Sehili 2006) reported almost complete disappearance of 2,4-D after 100 min. This was not apparent for the current study where 67 % of the original anionic form of 2,4-D would appear to have been converted to the free acid form after 105 min (also determined using a HPLC method). However Djebbar *et al.* (2006) used a florescence lamp emitting in the range 300-450nm as opposed to the current studies, where a medium pressure mercury UV lamp was used. A similar result was achieved by Djebbar with MCPA complete disappearance after 100 min.

This was not apparent for the current study where 59 % was again converted to the free acid after 105 min as determined by HPLC.

Djebbar *et al.* (2006) found the main intermediate for 2,4-D to be 2,4-DP. The decrease of the 2,4-D peak in the current study was due to the formation of the acid form of 2,4-D. It should also be noted that they observed the pH of their reaction mixtures decreasing as the reaction proceeded due to the formation of HCl. This finding correlates with the present study, as HCl is generated it is protonating 2,4-D, converting 2,4-D from its anionic form to its free acid form. In the current study the optimum pH (for 2,4-D photocatalysis) was found to be at natural pH of 3.3. Shanker *et al.* (2005) found this pH to also be the optimum for 2,4-D removal as the point of zero charge (pHzpc = -6.9) of $TiO_2$ which facilitates adsorption and dissociation of ions (Shankar *et al.* 2006).

In another study (Modestov and Lev 1998) it was found that 80 % of 2,4-D degradation occurred after 100 min. Irradiation was carried out with 300 W Xe lamp (280-400 nm). This study however used only a UV-Vis spectrophotometer for analyses and so could have missed other forms of 2,4-D that would be present in a HPLC chromatogram. Modestov *et al.* (1998) did perform TOC analyses where they calculated a TOC removal half-life of 13 hrs.

MCPA removal via $TiO_2$ photocatalysis in one study (Zertal, Sehili and Boule 2001) found that only 17 % of the initial concentration disappeared when stirred with $TiO_2$ under irradiation. They also found that at pH 5.9 the anionic form was almost quantitatively photohydrolysed.

The results of the current study show that $TiO_2$ photocatalysis does not completely degrade either 2,4-D or MCPA. While this finding appears to contradict the findings of some other studies (Djebbar, Zertal and Sehili 2006), it should be noted that the studies in the literature are not directly comparable because experimental conditions such as different light sources, reactor configurations and operating parameters varied as describe above among the different studies. The decrease in 2,4-D peak size may suggest degradation of a target analyte however in the current study we found that the target analyte still remained in a different form at a different retention time. $TiO_2$ photocatalysis has been used with the reactor configuration used in the current study to successfully degrade famotidine, indomethacin, and amoxicillin (Basha 2011).

These results may also explain the observed failure of the dolomite/$TiO_2$ composite. Based on the above results with $TiO_2$ it appears that acid is being generated under UV irradiation, the same must be true in the case with the $TiO_2$ composite. However, since $TiO_2$ is on the surface of a carbonate based mineral (dolomite) the acid that is being generated is being neutralised by the carbonate in the dolomite. Thus protonation of the analytes 2,4-D and MCPA does not occur, resulting in no observable change in the reaction mixture when analysed by HPLC.

## 6.3. Addition of hydrogen peroxide

In the current study $TiO_2$ photocatalysis was found to be efficient for the removal of the target analytes 2,4-D and MCPA but the AC/$TiO_2$ composite gave a more efficient removal of both analytes in shorter time period which is believed to be due to adsorption. In order to improve $TiO_2$ photocatalysis efficiency the addition of hydrogen peroxide to the system was investigated. The addition of hydrogen peroxide should prevent the recombination of positive holes and electrons by providing electron acceptors and therefore improving photodegradation (Wong and Chu 2003). Photocatalysis experiments with peroxide on its own and $TiO_2$ on its own were compared with the combination of both of these reagents as shown in Figure 6-8 and Figure 6-9 for MCPA and 2,4-D respectively.

For MCPA photocatalysis the combination of hydrogen peroxide and $TiO_2$ gave the best removal (92 %). $TiO_2$ photocatalysis for MCPA gave 88 % removal. Hydrogen peroxide on its own for MCPA only gave 49 % removal.

Interestingly, with 2,4-D, hydrogen peroxide photodegradation (on its own) very little removal (0.8 %) was achieved. The combination of hydrogen peroxide and $TiO_2$ (88 % at 280 min) for the removal of 2,4-D was less efficient than $TiO_2$ on its own (95 % at 300 min ). Initially the combination did give a faster degradation of 2,4-D when compared to $TiO_2$ on its own.

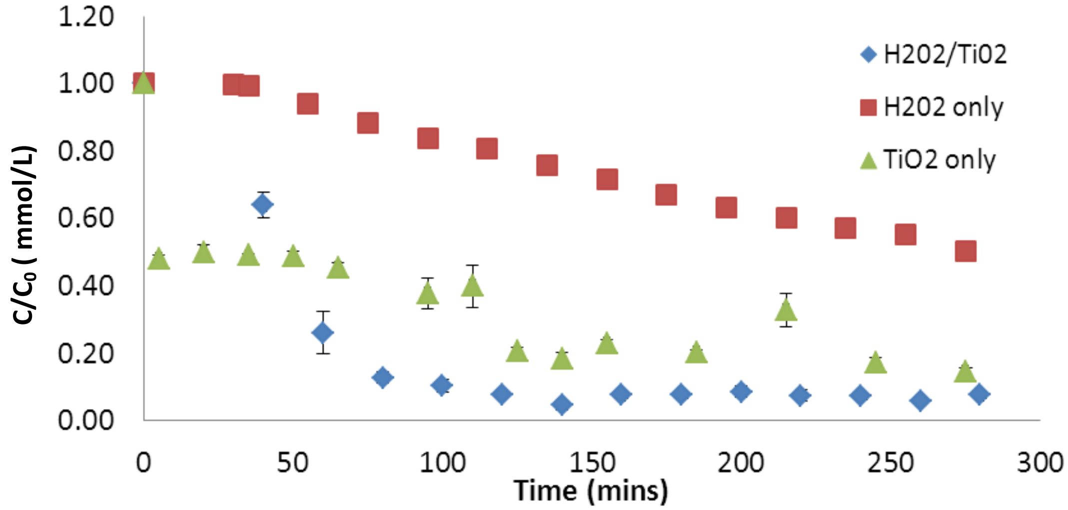


**Figure 6-8: MCPA Photocatalysis with $TiO_2$ only, $H_2O_2$ only and the combination of both $TiO_2$ and $H_2O_2$**

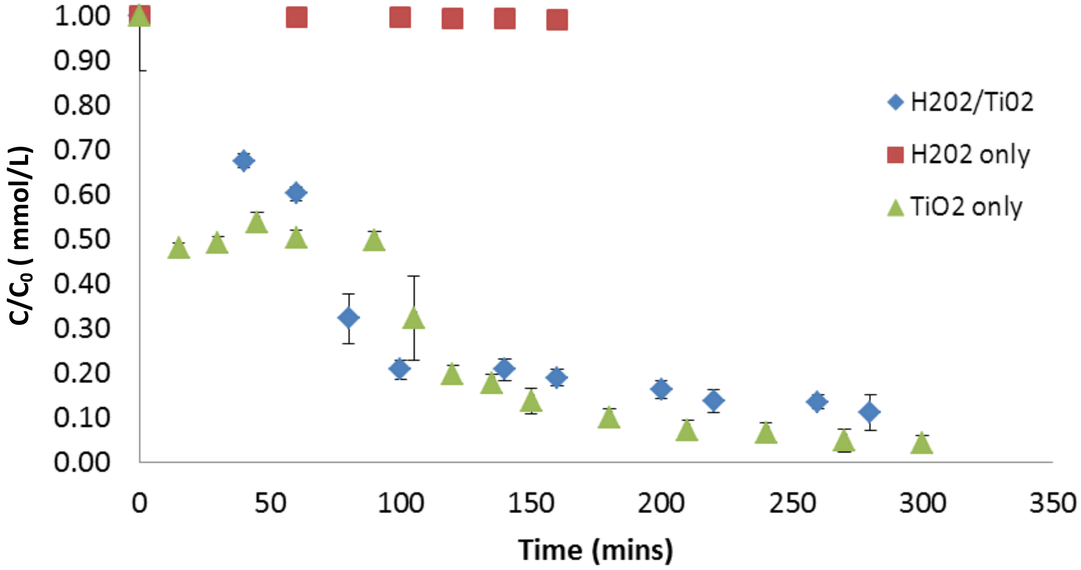


**Figure 6-9: 2,4-D Photocatalysis with $TiO_2$ only, $H_2O_2$ only and the combination of both $TiO_2$ and $H_2O_2$**

In another study (Wong *et al.* 2003), $H_2O_2$ and $TiO_2$ were used in combination under UV light to degrade the pesticide Alachlor (chlorinated aromatic). This study found that the addition of $H_2O_2$ at lower concentrations (up to 4.94 mmol/L) improved the photodegradation rate but at higher concentration it retarded the photodegradation rate. The improvement was attributed to the generation of free radicals by the direct photolysis of $H_2O_2$. At high $H_2O_2$ dosage, however, the excess $H_2O_2$ molecules were thought to be scavenging the HO• that was generated by either the direct photolysis of $H_2O_2$ or the photooxidation of OH- by h+ and were forming $HO_2$• (a much weaker oxidant). The major difference between this study (Wong *et al.* 2003) and the current study is that this study used monochromatic light at 300 and 350nm whereas the current study used a lamp that emitted light between 248 and 579 nm (Appendix 3 Figure A-11). Another difference is concentration of $H_2O_2$. This study used a $H_2O_2$ concentration of 4.94 mmol/L whereas the current study used 3 mmol/L. Wong *et al.* (2003) achieved 90 % TOC removal. The current study achieved 88 % 2,4-D removal in 280 mins whereas Wong achieved 90 % TOC(Alachlor) removal in 95 min.

A further study by Benitez *et al.* (2004) found that $H_2O_2$ and UV light successfully photodegraded (90 % removal) both MCPA and 2,4-D without the use of $TiO_2$. The major difference between this study and the current one is the light source. Benitez (2004) used a lamp which emitted monochromatic radiation at 254 nm whereas a lamp that emitted radiation between 248 nm and 579 nm was used in the current study. Another difference is the concentration of $H_2O_2$. Benitez used $2x10^{-3}$ M of $H_2O_2$ whereas the current study used $3x10^{-3}$ M.

To the best of the author's knowledge there is no published data available on the use of both $H_2O_2$ and $TiO_2$ for the removal of MCPA and 2,4-D. Advanced oxidation process studies tend to use either UV and $TiO_2$ or UV and $H_2O_2$ but not the combination of both.

# 7 Conclusions and Further work

## 7.1 Main findings and conclusions

This thesis investigates the development of $TiO_2$ composites for the removal of pesticides 2,4-Dichlorophenoxyacetic acid and 4-chloro-2-methylphenoxyacetic acid from water. A critical literature review describing background information on pesticides and the methods of removal of pesticides from water, including 2,4-D and MCPA was conducted (Chapter 2). This review identified a gap in the knowledge in this research area. While there have been a number of studies that examined the photodegradation of pesticides using Titanium Dioxide as the photocatalyst, there has been no research to date that looked at the degradation of pesticides using a combination of adsorption and photodegradation.

Experimental data was produced on both the adsorption process (activated carbon) as well the photodegradation ($TiO_2$) of the target analytes. $TiO_2$ photosensitisation was also conducted using dyes. New dolomite/$TiO_2$ composites were also investigated. Characterisation was performed on all three composites and all composites were evaluated for removal efficiency.

### 7.1.1. Composite preparation and characterisation

All composites were successfully prepared and optimised to produce the most effective and consistent batches of composite for removal of the target analytes. All composites were prepared successfully and characterised. The characterisation results showed that $TiO_2$ was present on all composite surfaces.

### 7.1.2. Adsorption studies

Sorption studies conducted were found to be consistent with previous work by the research group on a variety of target analytes and showed considerable adsorption of MCPA and 2,4-D onto AC and AC/$TiO_2$ with 90-99 % adsorption achieved. MCPA removal was enhanced (76 % removal) when adsorbing to AC when compared to 2,4-D (63 % removal) which can be explained by the difference in the log P values of 2,4-D and MCPA. MCPA and 2,4-D adsorption onto the AC/$TiO_2$ composite resulted in a similar adsorption pattern to one another. Adsorption models were applied to the data. The Freundlich model was found to be the best fit to the data for both analytes which was confirmed by statistics. Kinetic modelling showed that the composite data fitted well to a pseudo second order model initially but as adsorption slowed so did the effectiveness of the model fit to the data.

### 7.1.3. Photodegradation studies

#### AC/$TiO_2$ composite

The AC/$TiO_2$ system was optimised by investigating the following parameters; reactor volume, weight of composite, $TiO_2$ percentage in the composite, pH of composite and initial concentration of analyte. The 200 mL reactor was selected as this volume would result in less chlorinated waste being generated and therefore a reduction in waste costs. No apparent difference was noted between this volume and a 1 litre volume reactor. The optimum weight of composite used in photodegradation studies was determined to be 0.3 g as it gave the most efficient response (96 % removal). The 10 % $TiO_2$ loading composite was found to be the most efficient with a removal rate of 94 %. The pH of the composite in solution was investigated and it was established that the most efficient degradation was when the solution was at its natural pH (3.3). This was most likely due the pH of solution being near the pKa of the analytes. Above this pH there is a shift of the band edges of $TiO_2$ to more negative values. A 0.5 mM (100 ppm-110 ppm) initial concentration was chosen in order to obtain visible degradation curves.

Once the system was optimised the adsorption and photodegradation components of the composite were analysed. Control experiments were conducted in the dark, with unmodified activated carbon and $TiO_2$ and at various pH's (3.3, 4, 5, 6, and 10). Experiments conducted in the dark showed little difference (3.7 % standard deviation) to those conducted under UV irradiation. This showed that adsorption was the dominating process in the AC/$TiO_2$ composite as photodegradation only occurs under UV irradiance. The activated carbon controls were compared to 10 % composite experiments and no significant difference was noted therefore it was concluded that the majority of the removal was by adsorption. The $TiO_2$ controls showed that photodegradation could occur after an initial adsorption period prior to the switching on of the light. The 2,4-D $TiO_2$ control showed efficient degradation with 49 % adsorption in the dark, 48 % photodegradation with UV irradiation (248 -579 nm) yielding 97 % total 2,4-D removal. The MCPA $TiO_2$ control gave less photodegradation (33 %) but more adsorption (55 %). This is most likely due to the structure of MCPA, which has only one chlorine substituent and is therefore easier to degrade, compared to 2,4-D, which has two chlorine substituents making it more stable. The effect of pH on the $TiO_2$ controls was also investigated. It was determined that the optimum pH was the analytes natural pH (3.3). This is due to this pH being closest to the herbicides pKa.

Overall this study shows that AC/$TiO_2$ effectively removes 2,4-D and MCPA from water but only as adsorbents and do not work effectively at removing them permanently via photodegradation. The initial conclusion is that it is most likely due to the activated carbon being a black material and therefore absorbing all the light equally on its surface, making it very difficult for light to penetrate through the pores to activate the $TiO_2$ present in the composite.

### Dye/$TiO_2$ composites

The TCPP Porphyrin/$TiO_2$ composite was shown to work effectively at removing the pharmaceutical, famotidine under visible light by complete removal in 180 mins. $TiO_2$ on its own had a removal rate of 20 % but when combined with the TCPP it gave almost complete removal. This composite did not work effectively at removing 2,4-D and MCPA, where no degradation occurring within 3 hrs of illumination. This was due to the stability of the herbicides and that superoxide anion is not a strong enough oxidant to mineralise/oxidise either of the analytes.

A methylene blue/$TiO_2$ composite and a brominated porphyrin/$TiO_2$ composite were also developed but did not achieve degradation of the analytes. It was thought that these two composites do not work since the dye actually coats the $TiO_2$ with a thick layer of dye inhibiting the photochemistry.

## Dolomite/$TiO_2$ composite

Although dolomite had been found to effectively remove metal pollutants via adsorption it was not able to efficiently remove the target analytes as a maximum removal of only 7 % was achieved for 2,4-D removal and 15 % for MCPA at low concentrations only.

The dolomite/$TiO_2$ composite did not successfully remove the target analytes via photodegradation. However, this composite was found to be effective at removing the pharmaceutical famotidine with a 99 % removal rate (Gholamvand 2013) under UV irradiation, therefore it is photoactive. To develop a better mechanistic understanding of the dolomite/$TiO_2$ composite failure a series of control experiments were run using $TiO_2$ with both 2,4-D and MCPA under UV irradiation. This work revealed that under UV irradiation $TiO_2$ generates acid which protonates the analytes to their free acid form, with minimum degradation observed. Since dolomite is comprised of carbonate we believe that the photoactivity of the dolomite/$TiO_2$ composite is not being quenched. Instead we believe that the acid generated under UV irradiation by the $TiO_2$ on the dolomite surface is being neutralised by the carbonate based mineral, and therefore the analytes are not protonated to their neutral form - thus there is no apparent change in the reaction mixture.

## 7.2 Research Contributions

This study has attempted to make a contribution to the field of pesticide removal with use of $TiO_2$ composites. The main research contributions arising from this study are:

- **Knowledge gap -synergistic effect of adsorption and photocatalysis**

  There are a large amount of studies on the adsorption and photocatalysis of pesticides but very few that combine both of these components. This study looked at the target analytes adsorption onto activated carbon and to a lesser extent dolomite as well as examining the $TiO_2$ photocatalysis of the analytes.

- **More research on $TiO_2$ photocatalysis**

  There are a large number of papers published on the removal of pollutants via $TiO_2$ photocatalysis. There are a few which focus on pesticide removal and even fewer that look at the target analytes for this study. This study will help to fill this gap of knowledge.

- **Improved techniques for the detection of target analytes**

  This study also highlighted the importance of the analytical technique applied to detect analyte concentration. Some studies in the literature only use UV-vis spectrometry to detect compounds. We have found that this is not sufficient for the detection of the target analytes are the UV-Vis spectrophotometer does not separate compounds and therefore other breakdown products of the compound are not detected.

- **Recalcitrant compounds**

  This study highlighted the fact that both 2,4-D and MCPA are difficult to breakdown using the $TiO_2$ composites. They are relatively easily adsorbed from solutions but are not readily removed via photodegradation. Some published literature which claimed almost complete disappearance utilised different test systems with $TiO_2$ photocatalysis only. Parameters such as light source used, reactor configuration and pH of solution all affect the degradation of these compounds.

- **Photosensitisation**

  Photosensitisation of $TiO_2$ for the purpose of pollutant removal is a relatively recent area of study. Most literature in this area focuses on its use in solar cells. This study will add to the knowledge in the area of dye photosensitisation.

## 7.3 Future work

### 7.3.1. AC/$TiO_2$ composite Recyclability

The overall advantage of using this composite when compared to conventional activated carbon is that in theory the composites should be reusable due to the photodegradation of the adsorbed pollutants. The results of this project show that the composite does not work more effectively than using activated carbon on its own with 2,4-D and MCPA. If the composite can be recycled this would give merit to their use in large scale treatment facilities. However, this has not proven to be the case to date.

### 7.3.2 Wastewater photodegradation

As can be seen from the literature review (Chapter 2) most studies use laboratory water (ultra-pure/deionised water) in their experiments and this is not representative of real water matrices. Wastewater samples spiked with the pesticides could be used to represent real wastewater. Wastewater samples could also be taken at water bodies close to agricultural activities.

### 7.3.3. Other pesticides

Since the target analytes have proven difficult to remove, it would be interesting to see if other pesticides could be degraded using the same system with the three composites. These target analytes were chosen due to the fact that they are commonly applied in Europe and have been detected above their drinking water upper limits. Research has been conducted within our research group on these pesticides and so a knowledge base is available as well as validated method of detection. One pesticide of interest would be glyphosate since it is also commonly applied in the EU both commercially and residentially and does not contain chlorine or an aromatic ring and so may be easier to breakdown.

### 7.3.4. Light sources

The use of mercury vapour lamps for lighting purposes is due to be banned in the EU by 2015 due to their energy inefficiency and the toxicity of mercury (EC. 2003). Alternative light sources for these composites should be investigated. More energy efficient UV light sources as well as solar light (for dye/$TiO_2$ composite) could be investigated to reduce energy costs and inefficiency.

### 7.3.5 Dolomite as an adsorbent

Dolomite could be investigated as a cheaper alternative to AC. In order to manufacture activated carbon materials such as “coal, wood, coconut shell, bone, resins need to be subjected to reaction with gases, sometimes with the addition of chemicals, e.g. $ZnCl_2$, before, during or after carbonization in order to increase its adsorptive properties” (Verhoeven JW 1996). These processes are very costly. Dolomite has the advantage that it does not have to be activated using these processes. In addition to the cost savings this is also a more environmentally sound option, as straightforward calcination is sufficient for use as an adsorbent.

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# Appendices

## Appendix one: MS Data for 2,4-D $TiO_2$ photocatalysis

## Appendix two: MS Data for MCPA $TiO_2$ photocatalysis

## Appendix three: Emission spectra of UV lamp

# Appendix one: MS Data for 2,4-D $TiO_2$ photocatalysis

All the chromatograms shown here were taken from 2.4-D samples that had undergone $TiO_2$ photocatalysis. They are graphed in terms of intensity (Intens) versus mass to charge ratio (m/z). Tandem mass spectrometry analysis was also performed on some samples in order to determine fragment ions. The times denoted here are sample times when an aliquot of solution was retrieved from the photocatalysis reaction, filtered and analysed via direct infusion to the mass spectrometer. Zoom refers to an area on the chromatogram that has been magnified to enhance the smaller peaks.

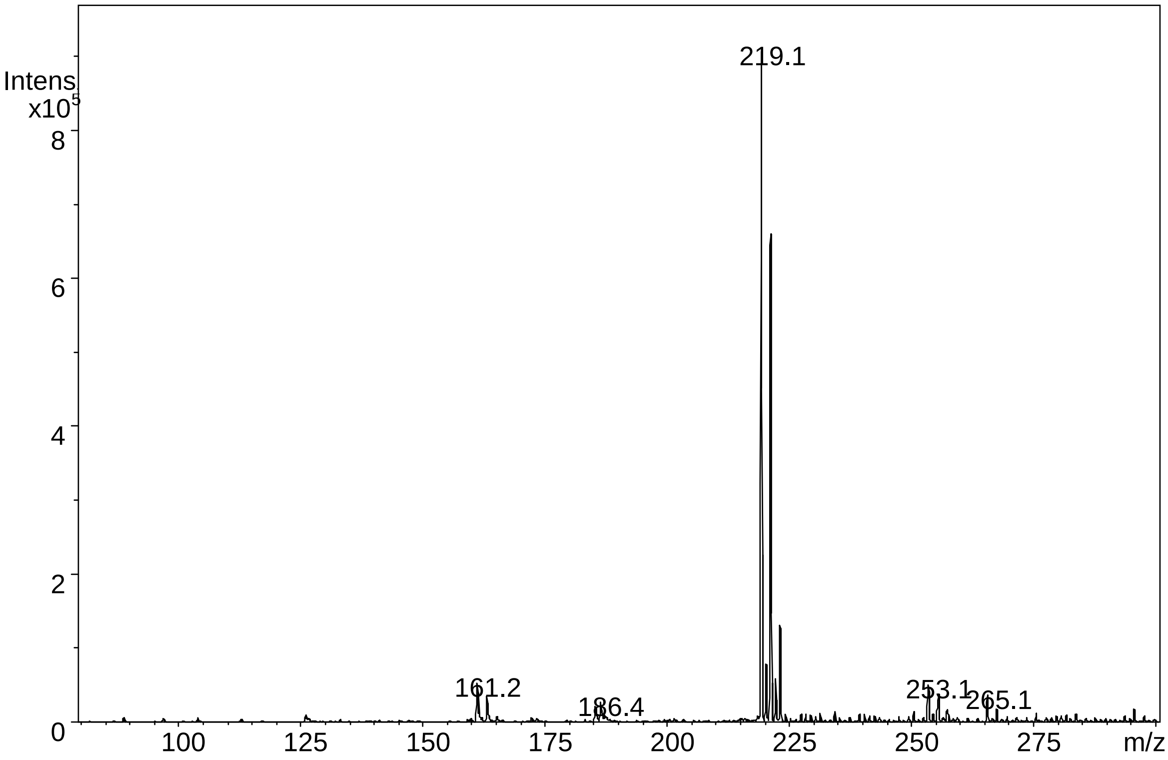

Figure A-1: MS chromatogram of 24-D $TiO_2$ photocatalysis at 60 min

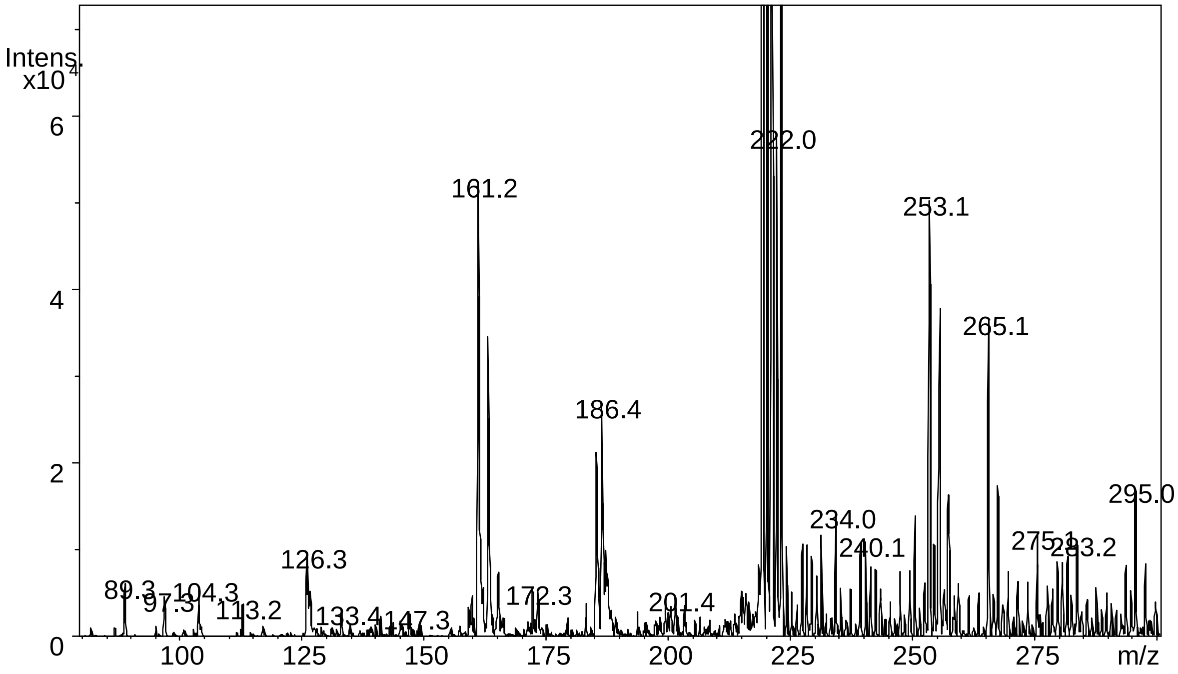

**Figure A-2: MS chromatogram of 24-D $TiO_2$ photocatalysis at 60 min (zoom)**

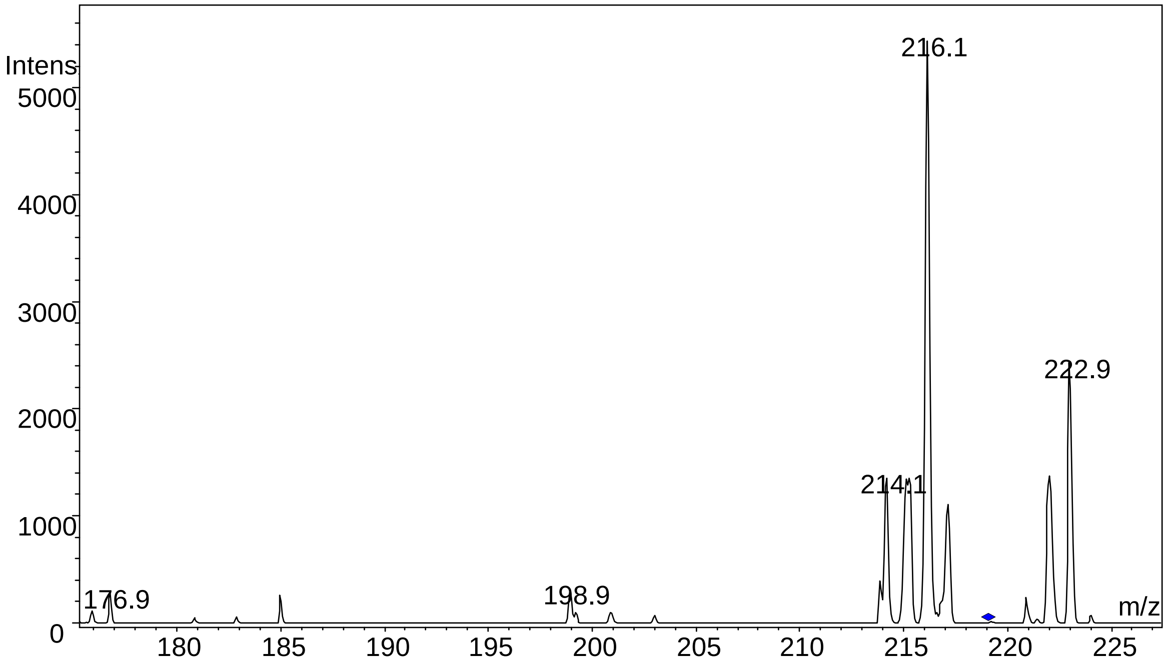

**Figure A-3: MS-MS chromatogram of 24-D $TiO_2$ photocatalysis at 60 min (parent ion 199)**

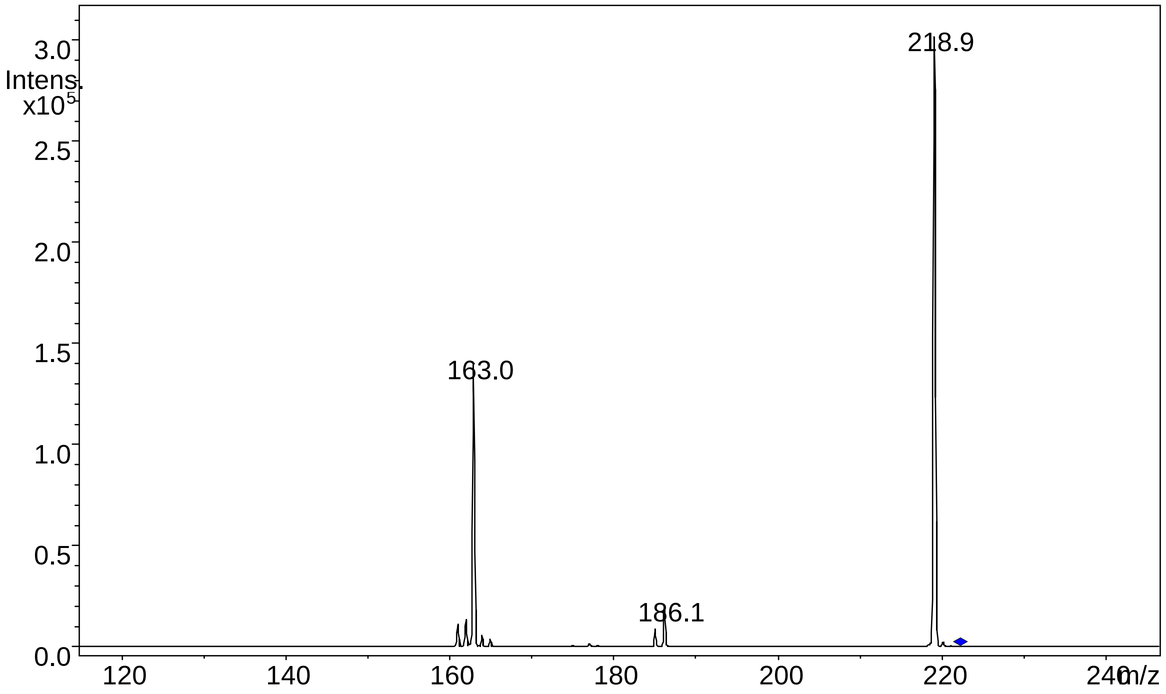

**Figure A-4: MS chromatogram of 24-D $TiO_2$ photocatalysis at 240 min**

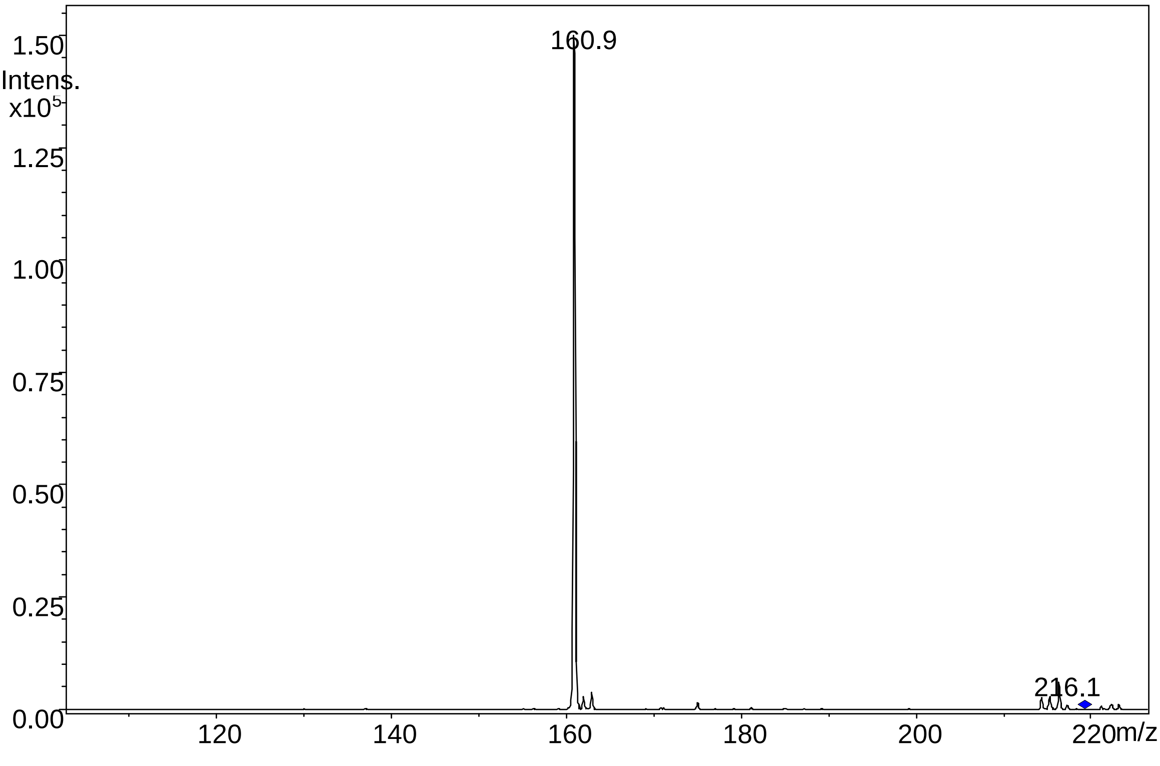

**Figure A-5: MS-MS chromatogram of 24-D $TiO_2$ photocatalysis at 240 min (parent ion 219)**

# Appendix two: MS Data for MCPA $TiO_2$ photocatalysis

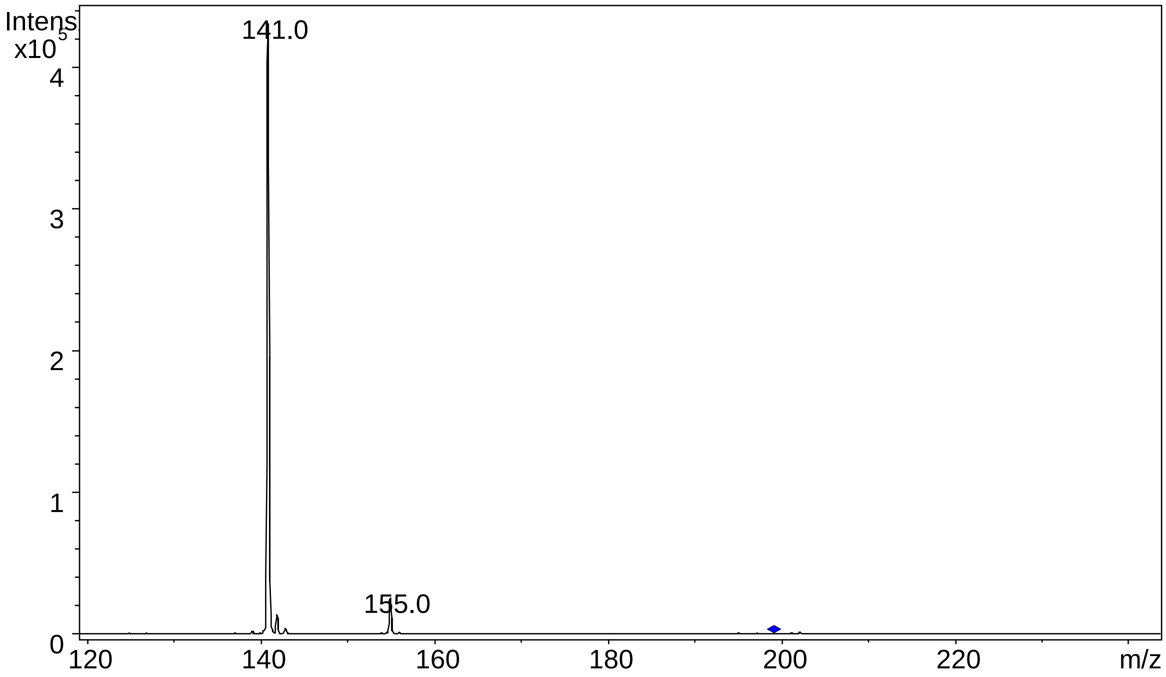

**Figure A-6: MS-MS chromatogram of MCPA $TiO_2$ photocatalysis at 60 min (parent ion 199)**

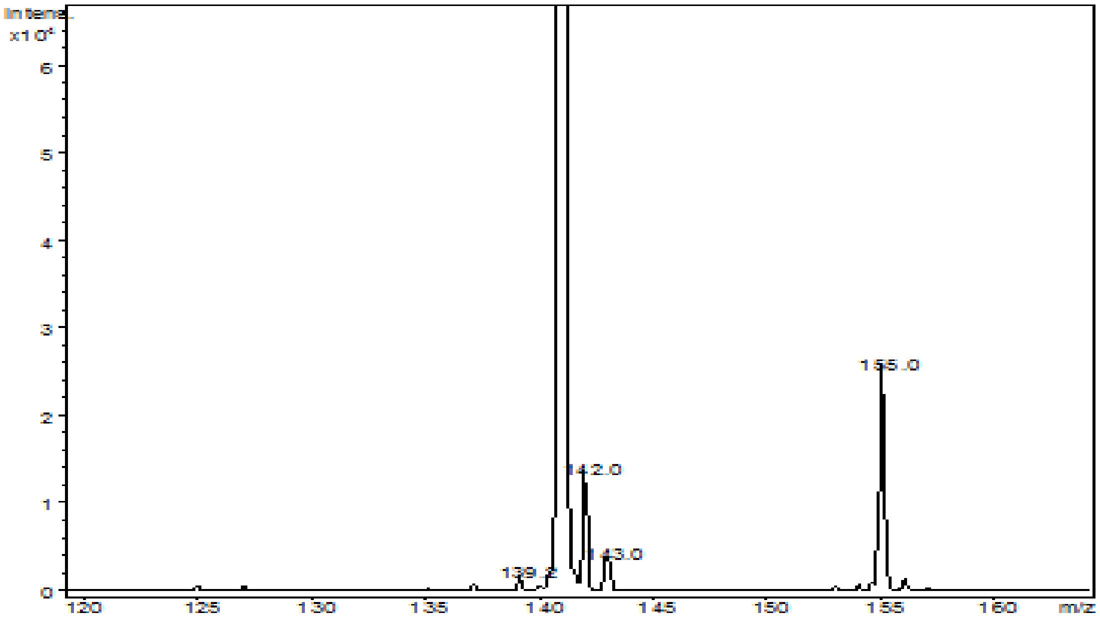

**Figure A-7: MS-MS chromatogram of MCPA $TiO_2$ photocatalysis at 60 min (parent ion 199) zoom**

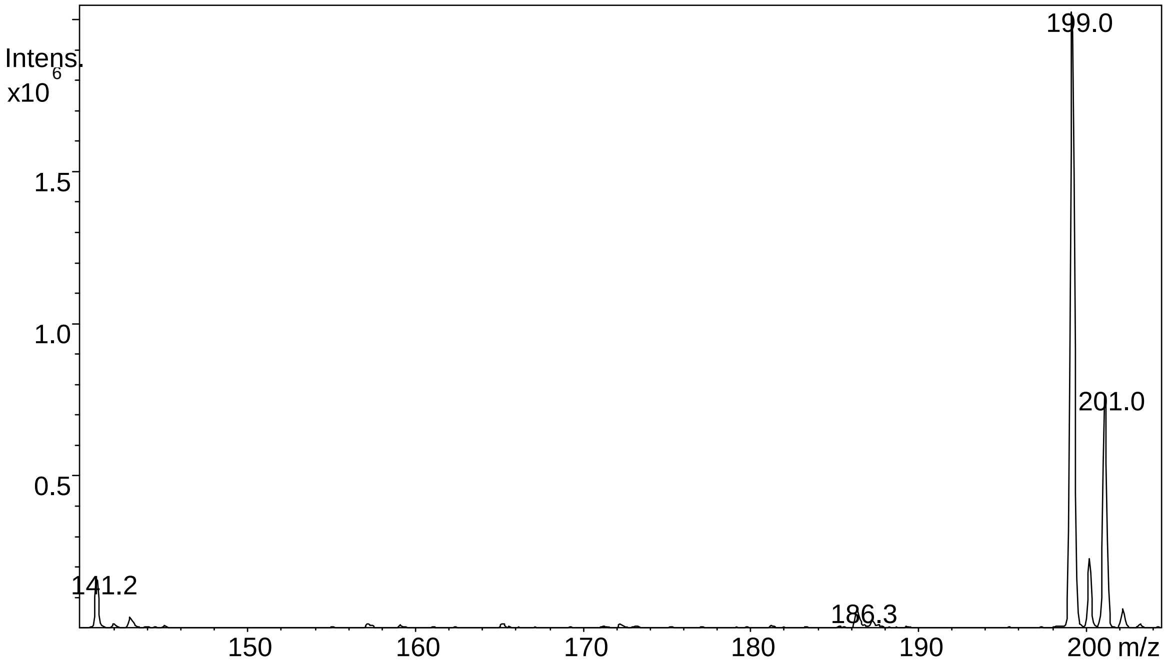

Figure A-8: MS chromatogram of MCPA $TiO_2$ photocatalysis at 240 min

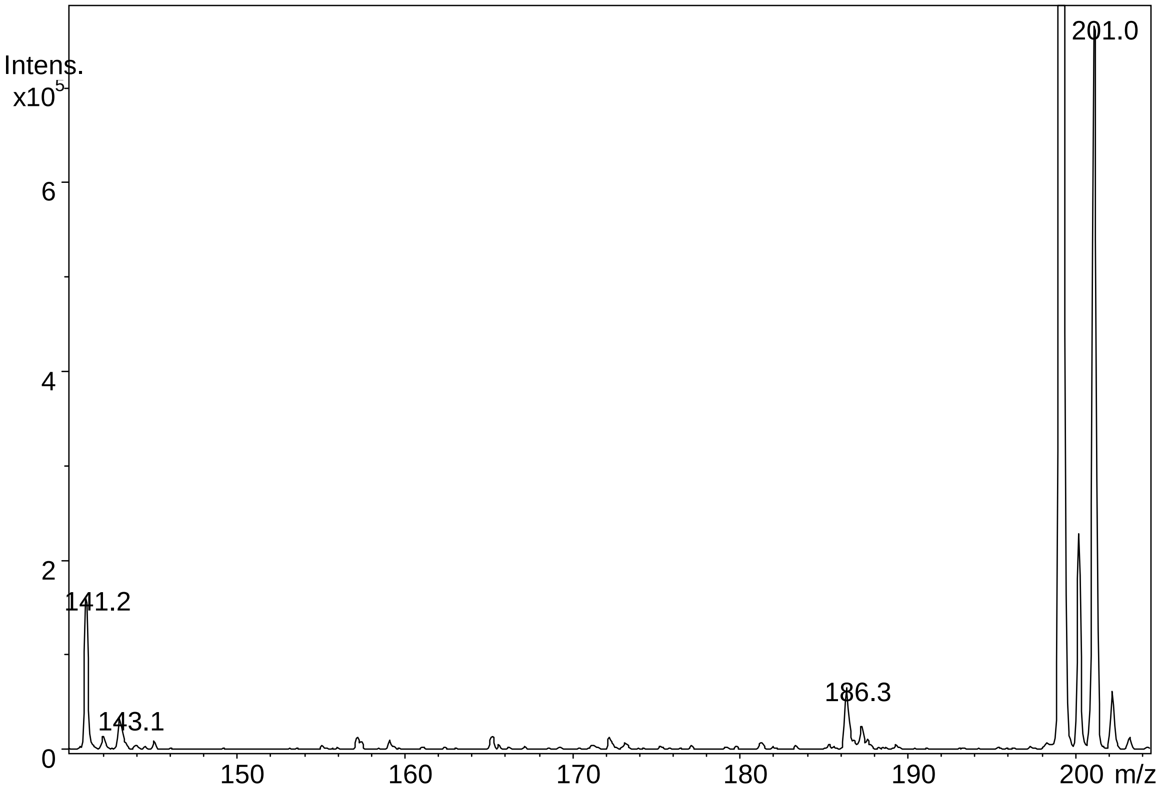

Figure A-9: MS chromatogram of MCPA $TiO_2$ photocatalysis at 240 min (zoom)

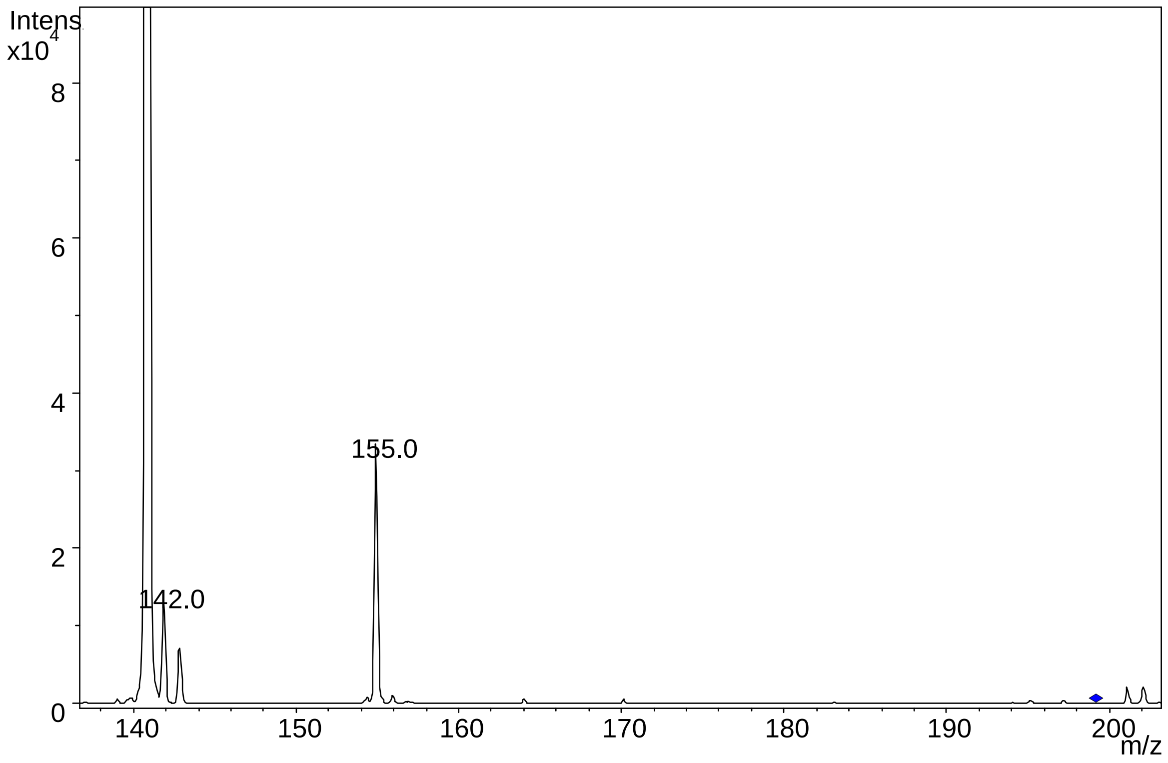

**Figure A-10: MS-MS chromatogram of MCPA $TiO_2$ photocatalysis at 240 min (parent ion 199)**

## Appendix Three: Emission spectra of UV lamp

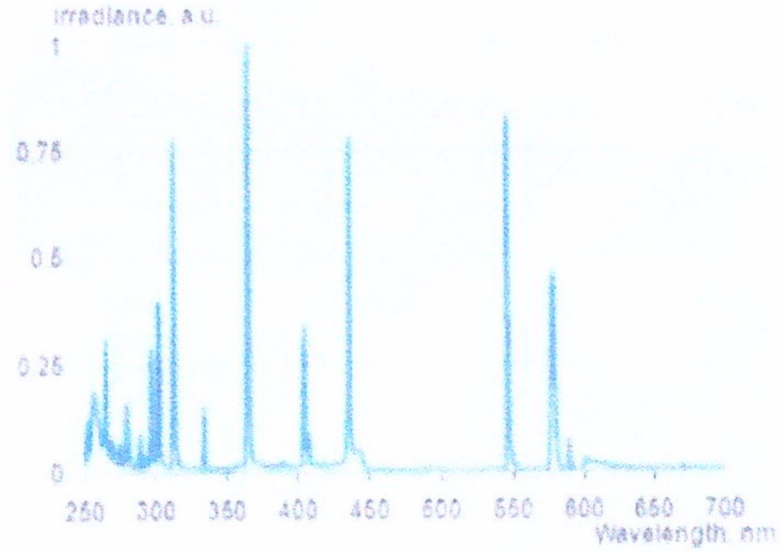

**Figure A-11 Test certificate provided by the manufacture for the medium pressure Hg lamp (TQ-150) used for all studies.**