CRANFIELD UNIVERSITY

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EVALUTION OF HYBRID SYSTEMS FOR TREATMENT OF EFFLUENTS FROM THE PESTICIDE PRODUCTION INDUSTRY

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MSc by Research
Academic Year: 2016 - 2017

Supervisors: Dr Ana Soares, Dr Irene Carra Ruiz
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ABSTRACT

The pesticide production industry generates a high strength wastewater containing a range of toxic pollutants (2,4-dichlorphenoxy acetic acid: 2,4-D; 4-(2,4-dichlorphenox) propionic acid: 2,4-DP; 4-(2,4-dichlorophenox) butyric acid: 2,4-DB; 2,4-dichlorophenol: 2,4-DCP; 2,4,6-trichlorophenol: 2,4,6-TCP; 4-chlororthocresol: PCOC; 4-chloro-2-methyl phenoxyacetic acid: MCPA, 4-(4-chloro-2-methylphenoxy) butyric acid: MCPB and 2-(4-chloro-2-methylphenoxy) propionic acid: MCPP). These pesticides can enter the natural environment and water sources if not removed in a wastewater treatment plant. Treated effluents are regulated by legislation such as the Water Framework Directive (WFD).

The organic matter and pesticides concentrations in the wastewater were highly variable across the 12 sampling campaign carried out. These results were expected, as the pesticide production facility manufactures different formulations at different intervals of time. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD) concentrations ranged from 5101-18000 mg/L and 18675-47763 mg/L, respectively. The pesticides average concentrations for 2,4-DCP were high at 58.96 mg/L, followed by MCPA at 32.45 mg/L, PCOC with 21.91 mg/L, 2,4-D at 13,94 mg/L and MCPP at 7.58 mg/L. On the other side the average concentrations for 2,4-DB and 2,4,6-TCP were >5 mg/L and the average concentrations for 2,4-DP and MCPB were <1 mg/L.

When evaluating different treatment options to design a hybrid system to treat the pesticide production industry wastewater it was clear that a biological treatment process should be considered due to the high BOD and COD. Anaerobic treatability tests indicated that the wastewater was toxic to organism present in anaerobic digested sludge, as no methane production was observed at dilutions >1%. Aerobic respirometry tests showed this wastewater was toxic to activated sludge microorganisms at dilutions >25%. Nevertheless, when testing the wastewater diluted to 25%, it was observed that the addition of nutrients (1.7 g/L NH_4 and 0.23 g/L PO_4) and alkalinity (and 0.1 g/L) enhanced the biological degradation, with pesticide removals of 63% for phenoxy acids (MCPB, MCPA, PCOC, MCPP), 34% for 2,4,6-TCP and 17% for dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP).. Acclimatisation studies were inconclusive.

The physical/chemical characterization of the key pollutants present in the pesticide production wastewater indicates their likelihood to be adsorbed (molecular weight >170 mg/L and Log K_{ow} >2.5). Tests completed with granular activated carbon (GAC) indicated high adsorption capacity for these pollutants as 1 g/L GAC removed 100% of the phenoxy acids, 2,4,6-TCP and dichloro acids within 24h. Lab-scale column tests were completed with pesticides breaking through between 599-1374 bed volumes (BV) when using 3-30 minutes EBCT. Advanced oxidation processes (AOPs) showed no removal of pesticides when treating the wastewater with Fenton process even at high doses of H_2O_2 (12500 mg/L) and Fe^{2+} (20 mg/L) Other tests were completed with UV/H_2O_2 using a dose of 1250 mg/L H_2O_2 and a UV intensity of 3 mW/cm^2 but low 30% total pesticides removal was also observed. On the other side, UV photolysis was a shown to be efficient at removing the pesticides without the presence of H_2O_2.

The GAC-biological hybrid system showed that after GAC treatment the pesticide production wastewater was not toxic to the aerobic microorganisms at 75% wastewater dilution. After 552 BV GAC and biological treatment, removal efficiencies were significant with overall pesticide removals of 86% (phenoxy acids), 98% (dichloro acids) and 83% (2,4,6-TCP). Nevertheless, the effluent quality produced by this process would not bet high enough to achieve the limits described in the WFD and the GAC would need frequent regeneration, leading to high operational costs.

A number of hybrid systems (granular activated carbon, membrane bioreactor and ultraviolet photolysis) were also investigated. The MBR-GAC pilot-plant showed very effective especially after dosing with additional nutrients and alkalinity. After diluting the wastewater to 25%, to prevent toxicity to the MBR process, and GAC, the removals reached 88% for COD, 72% for BOD and 86-99% for pesticides. Photolysis with UV showed promising results to replace the GAC, as the MBR-UV system achieved a total pesticides removal of 99-100%. The MBR-UV hybrid system generated an effluent with 5 µg/L MCPA, 1 µg/L MCPB, 7 µg/L MCPP, 22 µg/L PCOC, 39 µg/L 2,4-D, 0.75 µg/L 2,4-DP, 0.37 µg/L 2,4-DB, 5 µg/L 2,4-DCP and 5 µg/L 2,4,6-TCP. Nevertheless, even with high effectiveness of the MBR and UV system the effluent did not reach the discharge limits to meet WFD annual average environmental quality standards (EQS) for 2,4-D (0.3 µg/L) and MCPA (2 µg/L), just the EQS for 2,4-DCP (20 µg/L) and MCPP (18 µg/L) would be met. The EQS are set for environmental water quality and could be met if the treated wastewater is discharged to a water body that ensures 1:150 dilution, assuming that no 2,4-D is present in receiving water body.

Keywords: Activated carbon, activated sludge, advanced oxidation processes, biological treatment, chlorophenoxy herbicides, Fenton process, UV/H_2O_2, industrial wastewater treatment.

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LIST OF ABBREVIATIONS

AC	Activated carbon
AS	Activated sludge
ASP	Activated sludge processes
AOPs	Advanced oxidation processes
BAT	Best available technology
BOD	Biological oxygen demand
BV	Bed volumes
CAS	Conventional activated sludge
COD	Chemical oxygen demand
DEFRA	Department for environment, food and rural affairs
EA	Environmental agency
EC	European commission
EPA	Environmental protection agency
EQS	Environmental quality standards
GAC	Granular activated carbon
GC/MS	Gas chromatography/mass spectrometry
Hc	Henry’s coefficient
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
Kd	Sludge waster distribution coefficient
K_{oh}	Octanol/water coefficient
K_{ow}	Reactivity to hydroxyl radials
LOD	Limit of detection
MBR	Membrane bioreactor
MLSS	Mixer liquor suspended solids
MTBE	Methyl-tert-butyl ether
OPEX	Operating expense
OUR	Oxygen uptake rate
PAC	Powdered activated carbon
POPs	Persistent organic pollutants
SPE	Solid phase extraction
SRT	Sludge retention time
STW	Sewage treatment works
TMPH	Trimethylphenylammonium hydroxide
TOC	Total organic carbon
TSS	Total suspended solids
UV	Ultraviolet

VOC	Volatile organic compounds
VSS	Volatile suspended solids
WFD	Water Framework Directive
WWTPs	Wastewater treatment plants

▌Introduction

The application of pesticides offers a means for regulating organisms that compete with humans for food, minerals and vitamins or can cause damage livestock, crops and humans. Production of pesticides involves large volumes of man-made chemicals in factories all around the world. Throughout the process waste by-products and other chemical wastes are generated that must be treated before safe discharge to the environment.

Pesticide production wastewater varies from industry to industry depending on the formulations produced and scale of applications i.e. domestic to industrial. Table 1-1 shows typical characteristics of pesticide production wastewater. From existing studies carried out on pesticide production wastewater, it can be seen that there is great variability for example, pH has been reported to be extremely acidic at 0.5 (Sahu, 2014) to extremely alkaline pH 14 (Misra et al., 2013), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) have been reported in the range of 150-33750 mg/L and 30-11590 mg/L, respectively (Table 1-1). This huge variations proposes a challenge when trying to treat the wastewater as these contributing parameters are key to determining whether the pesticide wastewater can be biologically treated or not and if the wastewater composition changes frequently will the treatment be effective for each batch variation. For example, when the COD/BOD ratio is below 3, the wastewater is shown to have good biodegradability, above 3 indicates poor biodegradability. Table 1-1 shows that pesticide wastewater can have good biodegradability 2.33 (Misra et al., 2013) suggesting that a biological process could potentially treat the wastewater, however other pesticide wastewaters have been reported to have poor to very poor biodegradability 5-14.2 (IFC, 1998; Sahu, 2014) suggesting that biological process would have a very limited chance of working. Another important parameter that is of major relevance when recommending treatment processes are the total suspended solids. Based on the high concentrations of TSS measured at 1750 mg TSS/L (Sahu, 2014), it would be recommended to implement a solids separation process (such as settling tank, lamella settler or micro-screen). For low TSS, at 10 mg TSS/L (IFC, 1998), a separation process would not be as beneficial. Nutrients are essential when treating the wastewater biologically, without nutrients or minimal nutrients microbial growth would be limited. The recommended carbon:nitrogen:phosphate (C:N:P) ratio of 100:5:1 (Water Environment Federation, 2008) allows sufficient nutrients for the microorganisms to grow.

Table 1-1.Characterisation of different pesticide production wastewater.

pH	BOD (mg/L)	COD (mg/L)	Total suspended solids	Ammonium (mg/L)	Phosphate (mg/L)	COD/BOD	References
6.5	11590	33750	1437	19.1	2.5	3.08	This thesis Chapter 4
0.5-2	260	3680	1750	-	250	14.2	(Sahu, 2014)
6-9	30	150	10	-	-	5	(IFC, 1998)
4-5	750-1200	2500-5000	40-50	40-50	300-400	3.33-416	(Jin et al., 2010)
1.5-2.5	6100	33700	-	3080	2040	5.52	(Cheng et al., 2007)
2-8.5	37.2-49.5	124-366	-	-	-	3.33-7.39	(Barbusińs ki & Filipek, 2001)
12-14	2000-3000	6000-7000	250-300	-	-	2.33	(Misra et al., 2013)

The key pollutants in the pesticide production wastewater used throughout this study are; 2,4, dichlorphenoxy acetic acid (2,4-D); 4-(2,4 dichlorphenox) propionic acid (2,4-DP); 4-(2,4, dichlorophenox) butyric acid (2,4-DB); 2,4 dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy) butyric acid (MCPB) and mecoprop (MCPP) in the range of mg/L. These chlorinated herbicides (2,4-D, 2,4-DB, 2,4-DCP 2,4-DP, 2,4,6-TCP, PCOC, MCPA, MCPB and MCPP) have high molecular weights over 170 g/mol (except 2,4-DCP (163 mg/L) and PCOC (142.58 mg/L), Log Kd values mostly above 1.5 and an octanol/water partition coefficient (Log K_{ow}) over 2.5, indicating that these compounds have a hydrophobic nature and have a good adsorption capacity. These pesticides greatly vary in concentrations between each production sites. Concentrations of the above pesticides have been reported up to 2500 mg/L. The pesticides present in the wastewater in this study are highly variable with concentrations ranging from 0.1-107 mg/L. Studies of this strength of pesticides wastewater have been experimented using pilot or laboratory scale in order to remove the pesticides using different types of biological, physical and chemical treatment processes (Bernhard et al., 2006; Cheng et al., 2015; Mcallister et al., 1993; Vilar et al., 2012).

In order to correctly treat industrial wastewater, bespoke treatment is required to effectively remove the specific compounds to safe levels before being discharged to the environment. Recalcitrant pollutants which are not easily removed, such as pesticides, are treated to safe levels and are monitored for compliance to protect the environment. Regulators enforce effluent discharges consent limits to reduce levels of pollution in water courses (streams, rivers, sewers). Several organisations in the UK monitor the water quality, these include the European Union organisations (through the Water Framework Directive - WFD), the Department of Food & Rural Affairs (DEFRA) and the Environment Agency (EA) (Cirja, Ivashechkin, et al. 2008).

The treatment of pesticide production wastewater has been poorly described, but conventional wastewater treatment processes such as coagulation, filtration, trickling filters and activated sludge processes (ASP) have been used (Muller, et al., 2006; Mcallister et al., 1993; Soares, 2015). The application of biological processes to treat pesticide wastewater are often due to low capital and operational costs, though the process does not always remove the pesticides due to their recalcitrance, low water solubility or toxicity (Cirja et al., 2008; Lapertot et al., 2006). Hence, these processes do not continuously provide reliable effective treatments against pesticides. For instance, many studies have conveyed biological processes to be challenging when treating high strength wastewater due to pollutants showing toxicity and resistance towards the microorganisms (Jin et al., 2010; Oller et al., 2011). The chlorinated herbicides present in the wastewater under investigation 2,4-D, 2,4-DCP, 2,4,6-TCP, MCPA and MCPP will be challenging to remove using biological processes due to the structure, chemical groups and significant half-lives, therefore a pre/post treatment option would ensure that these chlorinated herbicides would be removed prior to being discharged (Fontmorin et al., 2013).

Granular activated carbon (GAC) is one of the best available technology (BAT) for organic compound removal in water due to been highly efficient at treating a wide range of organic compounds including pesticides (Evoqua Water Technologies, 2016). Studies show when utilising GAC as a pre-treatment process the adsorption of pesticides on GAC are decreased due to high competition with other bulk organic matter for adsorption pores. This can lead to reduced lifespan and increased frequency of media regeneration which makes the process very expensive. Literature suggests using GAC as a post-treatment increases the efficiency for adsorbing pesticides since most of the bulk organic matter will be removed prior to using GAC (Nguyen et al., 2012). Combining membrane bioreactor (MBR) and GAC to create a hybrid system would produce an even more enhanced high quality effluent, as the no suspended solid effluent with a lower concentration of organic matter and so suspended solids from the MBR would allow the GAC to target and remove the remaining recalcitrant pollutants (Melin et al., 2006).

The application of chemical processes such as advanced oxidation processes (AOPs) has also been used as another option in removing recalcitrant pesticides in wastewater. AOPs have received significant attention for the removal of pollutants in both industrial and domestic wastewaters (Badawy et al., 2006; Barbusiński et al., 2001; Irmak et al., 2004; Irmak et al., 2006; Kowalska et al., 2004; Lafi et al., 2006; Mokrini et al., 1997) due to the highly efficient treatments on recalcitrant wastewater. AOPs achieve this by generating hydroxyl radicals which are non-selective and highly reactive (Comninellis et al., 2008; García-Montaño et al., 2006; Lafi et al., 2006). Laboratory and pilot scale systems have been described by Irmak et al. (2004), Kowalska et al. (2004), and Barbusiński et al. (2005) using UV/TiO_2, UV/H_2O_2 and Fenton process, respectively showing pesticide removals between 51 to 100%. Ultra-violet and hydrogen peroxide have been scaled up whereas Fenton process can be scaled up but there is little existing literature on this.

Research to date has been focused on pesticide degradation in mixtures of one to four different pesticides; the more common pesticides 2,4-D, 2,4-DCP, MCPA and PCOC (Fontmorin et al., 2013; Irmak et al., 2004; Kowalska et al., 2004; Mcallister et al., 1993; Quan et al., 2004). Many laboratory scale studies using different types of wastewater with pesticides ranging from <0.36 µg/L (domestic wastewater) up to 2500 mg/L (landfill leachate) (Bernhard et al., 2006; Mcallister et al., 1993). The aim of this study was to establish the most suitable process to treat a pesticide production wastewater in order to achieve compliance with the effluent discharge limits set by environmental quality standards (EQS). A number of different biological, physical and chemical processes were evaluated and combined in hybrid processes to obtain an effective treatment option. Furthermore, results from this study can offer awareness and understanding on treatability of other types of pesticide wastewater.

1.1 Project Aim

The aim of this project was to develop a hybrid process combining biological, physical or chemical processes for treatment of pesticide production wastewater that was suitable to ensure delivery of high quality treated wastewater before it was released into the environment.

1.2 Objectives

1. Characterise the pesticide production wastewater and complete a desk based assessment on the commercial available options.
2. Complete treatability tests using biological, chemical and physical processes.
3. Combine the investigated processes to produce a successful hybrid treatment to pre-set consent/scenarios.

1.3 Thesis Plan

The project took 12 months to complete and was based on the 4 tasks.

Task 1

Characterisation of historical data and high performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC/MS) method development. This involved carrying out sampling every 3 weeks for a total of 12 sampling campaigns. For this, HPLC and GC-MS method development was required to analyse the compounds in the pesticide production wastewater.

Task 2

Desk based study on treatability options. This involved studying the chemical/physical properties of each key pollutant in the pesticide production wastewater to determine the environmental fate of each pollutant by studying; functional group, molecular weight, structure, solubility in water, ability to be adsorbed (Log K_{ow}, Log Kd), Henry's coefficient (Hc) and ability to react with hydroxyl radicals (Log K_{oh}). Most studies found in literature focused on synthetic solutions, synthetic wastewater, at lab-scale or pilot-scale. Although these studies can provide information on the removal mechanisms and provide a comparison between process efficiency, they have limited practical applicability. The process that has been more widely used to treat high strength wastewaters rich in recalcitrant compounds at full-scale, is the combination of biological/GAC and GAC/biological processes. The pesticide production wastewater contains a variety of compounds, that can be removed by 80-90% using biological processes (such as MBR) and GAC has been shown to selectively remove the pesticides, potentially creating a high quality effluent. Nevertheless, in order to assert processes design, efficiencies or costs, it is crucial to evaluate these processes experimentally.

Task 3 was about testing treatment options (biological, physical and chemical processes) and using data from task 1 to determine process efficiency at lab-scale. Experiments included respirometry, addition of nutrients and alkalinity, acclimatisation of the activated sludge, anaerobic treatability, GAC (equilibrium sorption time and regeneration), AOPs (UV/H_2O_2 and Fenton).

Task 4 was about combining the most effective removal processes from task 2 to produce a successful hybrid treatment process that would meet consent/scenarios. This involved a membrane bioreactor (MBR) with GAC adsorption process and photolysis with UV. GAC was experimented as a pre-treatment and post-treatment to determine the most efficient way of treating the pesticide production wastewater. Respirometry experiments were completed on pesticide production wastewater that was treated with GAC to determine the toxicity of the wastewater towards microorganisms.

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█ Literature Review – Commercially available treatment options to treat pesticide production wastewater

2.1 Introduction

According to the European Commission (EC) a pesticide is any substance or a mixture of substances that are intentionally used for the purpose of destroying, repelling, preventing or migrating any pest; used as a plant regulator, desiccant or defoliant or used as a nitrogen stabiliser (EC, 2016). Pesticides provide a way for regulating organisms that compete with humans for food, vitamins and minerals and prevent damage to crops, livestock and humans. In today's society pesticides have a major role in the economic production of farming and contribute to a large-scale success in the agricultural industry worldwide (USGs, 2005).

Pesticide production takes place in centralised factories involving the synthesis and combination of large volumes of man-made chemicals. During the pesticide production process waste products are formed giving origin to wastewater that needs further treatment before it is released to the environment. The characteristic of the pesticide production wastewater varies from company to company depending on the target crop and scale of applications such as domestic to industrial. For example, in the agricultural industry the chemicals are likely to be stronger and more hazardous when compared to domestic application such as a small garden.

Industrial wastewater requires bespoke treatment to successfully remove the specific compounds to safe levels before being discharged to the environment. Compounds which are not as easily removed such as pesticides are treated to safe levels and are monitored for compliance to protect the environment. This is achieved by reducing the quantity of pollution distributed in the environment with very strict limits. For example, for fresh water sources some recalcitrant pesticides have their own specific limits. For 2,4- dichlorophenoxyacetic acid (2,4-D) the limits are 0.3 µl/L (mean) and 1.3 µl/L (95 percentile) (Defra, 2014). In order to regulate and maintain safe levels of pollution in water courses (streams, rivers, sewers) several organisations in the UK monitor the water quality, these include the European Union organisations (through the Water Framework Directive - WFD), the Department of Food & Rural Affairs (DEFRA) and the Environment Agency (EA) (Cirja, Ivashechkin, et al. 2008).

The majority of research to date has been focused on pesticide degradation in mixtures of one to four different pesticides; the more common pesticides 2,4, dichlorphenoxy acetic acid (2,4-D), 2,4 dichlorophenol (2,4-DCP), 4-chloro-2-methyl phenoxyacetic acid (MCPA) and 4-chlororthocresol (PCOC) (Fontmorin et al., 2013; Irmak et al., 2004;

Kowalska et al., 2004; Mcallister et al., 1993; Quan et al., 2004). Studies using synthetic pesticide wastewater at laboratory scale have been shown to treat pesticide concentrations in the range of 0.9 – 20,000 µg/L (Moreira et al., 2012) whilst studies using different types of wastewater with pesticides at laboratory scale have been shown to treat pesticides ranging from <0.36 µg/L up to 2500 mg/L (Bernhard et al., 2006; Mcallister et al., 1993). The objective of this study was to establish the most suitable process to treat a pesticide production wastewater. A number of different biological, physical and chemical processes were evaluated and combined in hybrid process to obtain an effective treatment option. Furthermore, results from this study can offer awareness and understanding on treatability of other types of pesticide wastewater.

2.2 Current pesticide production wastewater treatment

Wastewater containing pesticides have been reported to be treated using conventional wastewater treatment processes such as coagulation, filtration, trickling filters and conventional activated sludge (AS) (Mcallister et al., 1993; Soares, 2015). Conversely, these processes do not provide reliable effective treatment against pesticides. For instance, many studies have reported biological processes to be challenging when treating high strength wastewater due to pollutants showing toxicity and resistance towards the microorganisms (Jin et al., 2010; Oller et al., 2011). The chlorinated herbicides 2,4-D, 2,4-DCP, 2,4,6-TCP, MCPA and MCPP will be challenging to remove using biological processes due to the structure, chemical groups and significant half-lives, therefore a pre/post treatment option would ensure that these chlorinated herbicides would be removed prior to been discharged (Fontmorin et al., 2013).

According to the US Environment Protection Agency (EPA) the best available technology (BAT) for organic compound removal in water is GAC due to being highly efficient at treating a wide range of organic compounds including pesticides (Evoqua Water Technologies, 2016). Studies show when utilising GAC as a pre-treatment process the adsorption of pesticides on GAC is decreased due to high competition with other bulk organic matter for adsorption pores. This can lead to reduced lifespan and increased frequency of media regeneration which makes the process very expensive. Literature suggests using GAC as a post-treatment increases the efficiency for adsorbing pesticides since most of the bulk organic matter will be removed prior to using GAC columns (Nguyen et al., 2012). Combining membrane bioreactor (MBR) and GAC to create a hybrid system would produce an even more enhanced high quality effluent, as the effluent with a lower concentration of organic matter and no suspended solids from the MBR would allow the GAC to target and remove the remaining recalcitrant pollutants (Melin et al., 2006).

The use of chemical processes offers an alternative option in removing recalcitrant pesticides in wastewater via chemical oxidation; for instance advanced oxidation processes (AOPs). Over recent decades AOPs have received significant attention for the removal of pollutants in both industrial and domestic wastewaters (Badawy et al., 2006; Barbusiński & Filipek, 2001; Irmak et al., 2004; Irmak et al., 2006; Kowalska et al., 2004; Lafi & Al-Qodah, 2006; Mokrini et al., 1997) due to the highly efficient treatments on recalcitrant wastewater. Advanced oxidation processes are able to achieve this by generating hydroxyl radicals which are non-selective and highly reactive (Comninellis et al., 2008; García-Montaño et al., 2006; Lafi & Al-Qodah, 2006) Removals between 51.4% to 100% removal have been achieved utilising various AOPs including UV/TiO_2 (Irmak et al., 2004), UV/H_2O_2 (Kowalska et al., 2004) and Fenton process (Barbusiński, 2005; Barbusiński & Filipek, 2001).

Although pesticides are produced in very large quantities worldwide, there is very little information about the production wastewater characterisation as well as reports on how to treat such a wastewater efficiently and economically. The aim of this review was understand the state of the art on the commercial available options to remove 9 pesticides (phenoxy acids and dichloro acids) from a high strength industrial wastewater from the pesticide production industry.

2.3 Treatment of Pesticide production wastewater

2.3.1 Chemical and physical properties of the chlorinated aromatic herbicides in pesticide production wastewater

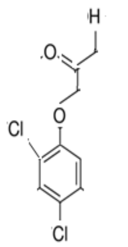
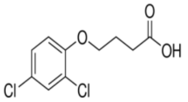
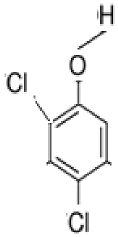
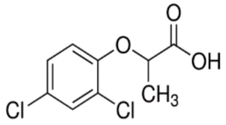
The chlorinated aromatic herbicides present in the pesticide production wastewater have different chemical and physical characteristics meaning they have different environmental fates. To understand and predict the most efficient processes to remove pollutants from wastewater, it is key to correlate the chemical and physical characteristics (Table 2-2) of the pollutants with their environmental fate such as solubility, molecular weight, structure octanol/water coefficient (Log K_{ow}), sludge distribution coefficient (Kd), Henry's coefficient (Hc) and compounds reactivity to hydroxyl radicals (K_{oH}). Table 2-1 presents an interpretation of the chemical and physical characteristics. Furthermore, these characteristics can help design suitable treatment processes using one or a combination of these: sorption, volatilisation, biodegradation and transformation or chemical conversion.

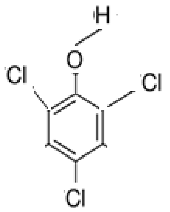
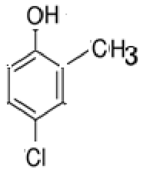
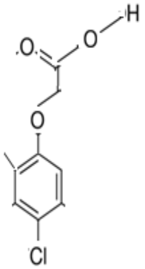
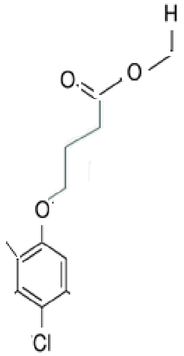
Table 2-2 was generated using existing literature to present physical and chemical characteristics for the pollutants for the following constants; solubility, Log K_{ow}, Kd, Hc, as well as the molecular weight and structure. These chlorinated herbicides (2,4-D, 2,4-DB, 2,4-DCP 2,4-DP, 2,4,6-TCP, PCOC, MCPA, MCPB and MCPP) have high molecular weights over 170 mg/L (except 2,4-DCP (163 mg/L) and PCOC (142.58 mg/L)), Log Kd values mostly above 1.5 and an octanol/water partition coefficient (Log K_{ow}) over 2.5, indicating that these compounds have a hydrophobic nature and have a good adsorption capacity (Table 2-1). Therefore using a physical adsorption treatment such as granular activated carbon (GAC) could potentially remove the compounds in the wastewater. Chemical treatment processes such as advanced oxidation processes (AOPs) could potentially be used to treat the chlorinated herbicides as the compounds reactivity to hydroxyl radials (K_{oH}) are around 10^9 1/M.s. However the fate of compounds with K_{oH} values between 10^9 – 10^{11} 1/M.s are hard to interpret and experimental trials are frequently needed.

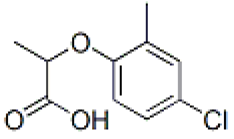
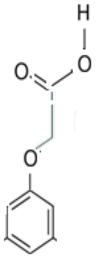
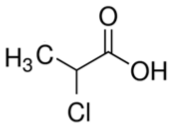
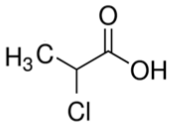
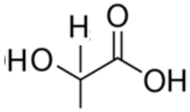
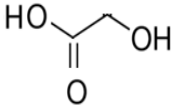
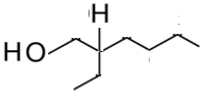
Table 2-1. Interpretation of the physical and chemical characteristics of pollutants.

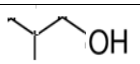
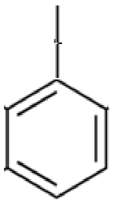
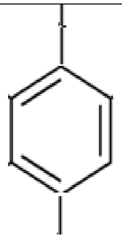
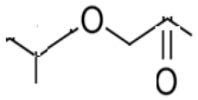
Solubility (mg/ L)	< 2 poor solubility	2-100 average solubility	>100 high solubility
Log K_{ow}	0.5 - 2.5 Very hydrophilic & bioavailable	2.5 - 4.0 Average hydrophobic	>4.0 Very hydrophobic
Log Hc (atm/mol.m^3)	< 10 -3 Volatilise	>10 -3 Poor volatilisation	
Log Kd	<0.7 - 1.5 Poor sorption to solids	0.1 - 10 Average sorption to solids	3.0 - 3.9 Strong sorption to solids
Log K_{OH} (1/M.S)	<10^9 Poor reactivity with hydroxyl radicals	>10^9 Good reactivity with hydroxyl radicals	

Table 2-2. Chemical and physical properties of the chlorinated aromatic herbicides present in the pesticide production wastewater.

CAS Number	Compound name	IUPAC name	Chemical formula	Configuration	Molecular weight (g/mol)	Solubility (mg/L)	Log Kow	Log Kd	Hc atm/(mol.m^{3})**	(K_{oh}) Reactivity between hydroxyl radicals (1/M.s)
94-75-7	**2,4, dichlorphenoxy acetic acid**	2,4-D	$C_8H_6Cl_2O_3$		221.04	890	2.61	2.95	5.81x10^{-9}	5.1x10^{9}
94-82-6	**4-(2,4, dichlorophenox) butyric acid**	2,4-DB	$C_{10}H_{10}Cl_2O_3$		249.09	4385	3.53	N/A	2.29X10^{-9} (non - volatile with water)	N/A
120-83-2	**2,4 dichlorophenol**	2,4-DCP	$C_6H_4Cl_2O$		163.00	4500	2.80	1.8	5.5x10^{-6}	5.5x10^{9}
120-36-5	**4-(2,4 dichlorphenox) propionic acid**	2,4-DP	$C_9H_8Cl_2O_3$		235.06	230	3.26	-1.5	9.0x10^{-7}	6.614 × 10^{9}

88-06-2	**2,4,6-trichlorophenol**	2,4,6-TCP	$C_6H_2Cl_3OH$		197.45	800	3.38		$2.3X10^{-7}$	$6.3x10^{09}$
1570-64-5	**4-chlororthocresol/4-chloro-o-cresol/para-Chloro-ortho-cresol**	PCOC/ 4CL2MPHE	C_7H_7ClO		142.58	2300	3.09	0.008	1.1X10-6	N/A
94-74-6	**4-chloro-2-methyl phenoxyacetic acid**	MCPA	$C_9H_9ClO_3$		200.63	630	3.25	1.47	$6.55x10^{-7}$	$6.6x10^{9}$
94-81-5	**4-(4-chloro-2-methylphenoxy) butyric acid**	MCPB	$C_{11}H_{13}ClO_3$		228.67	48	3.5	2.79	$3.22x10^{-4}$ Pa m3 mol-1	N/A

93-65-2	**2-(4-chloro-2-methylphenoxy) propionic acid**	MCPP	$C_{10}H_{11}ClO_3$		214.65	650	3.38	-1.5	$1.2x10^{-7}$	N/A
122-59-8	**phenoxyacetic acid**	PAA	$C_8H_8O_3$		152.15	1000-5000	1.34		N/A	N/A
29617-66-1	**α-chlorpropionic acid**	ACPA/2-chloropropanoic acid	$C_3H_5ClO_2$		108.52	freely soluble	0.76		$2.6X10^{-7}$	N/A
29617-66-1	**i-chlorpropionic acid**	LCPA/(S)-2-chloropropionic acid	$C_3H_5ClO_2$		108.52	freely soluble	0.76		$2.6X10^{-7}$	N/A
50-21-5	**lactic acid**	2-hydroxypropanoic acid	$C_3H_6O_3$		90.08	100000	-0.62		9.6×10^{-9}	N/A
79-14-1	**glycolic acid**	2-Hydroxyethanoic acid	$C_2H_4O_3$		76.05	100000	-1.11		1.09×10^{-4}	N/A
104-76-7	**2-ethylhexanol**	2-ethylhexan-1-ol	$C_8H_{18}O$		130.23	1000	2.9		$2.6X10^{-5}$	N/A

71-36-3	**n-butanol**	butan-1-ol	$C_4H_{10}O$		74.12	68000	0.88		6.3x10^{-6}	N/A
78-83-1	**i-butanol**	isobutanol/2-methylpropan-1-ol	$C_4H_{10}O$		74.12	68000	0.88		6.3x10^{-6}	N/A
108-88-3	**toluene**	Toluene	C_7H_8		92.14	526	2.73		6.64x10^{-3}	N/A
1330-20-7	**total xylenes**	dimethylbenzene	C_8H_{10}		106.16	198	3.15		7.18x10^{-3}	N/A
108-21-4	**isopropyl acetate**	propan-2-yl acetate	$C_5H_{10}O_2$		102.13	31900	1.28		2.78X10^{-4}	N/A

2.3.2 Biological Treatment

Biological processes are often used to treat industrial wastewater due to low operational and capital costs. However microorganisms are not always able to remove pesticides due to their recalcitrance, low water solubility or toxicity (Cirja et al., 2008; Lapertot et al., 2006). Organic pollutants can be degraded biologically either aerobically or anaerobically (Zheng, Zhao, Zhou, Fu, & Li, 2013).

[redacted] Aerobic treatment

Aerobic degradation of di-chlorinated pesticides, such as 2,4-D, is well understood, as these compounds have been released to the environment since the 1950's (Maltseva, McGowan, Fulthorpe, & Oriel, 1996). Aerobic breakdown usually takes place by oxidation and cleavage of the esther bond and chlorophenol hydroxylation. The formed chloro-cathechol would then be modified by an ortho-cleavage pathway. Once the aromatic ring is open, the chlorinated acetate compound can be used in the normal microbial metabolism, the tricarboxylic acid cycle, and transformed into carbon dioxide and water (Figure 2-1).

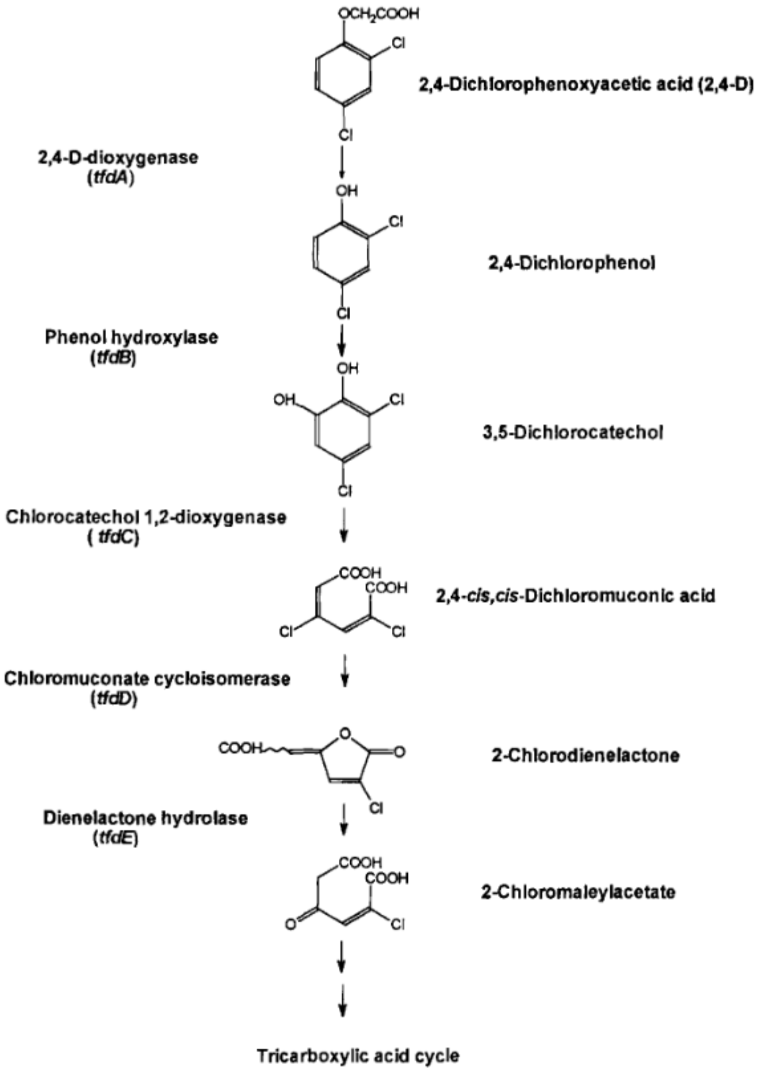


Figure 2-1. Aerobic pathway degradation of dichlorophenoxy acids (2,4-D) (from Maltseva et al., 1996).

[redacted] Activated sludge processes

Although activated sludge processes are often used to treat low strength wastewater that contains BOD and COD <1000 mg/L (Grady et al, 2011), these processes, have been shown to be suitable to treat industrial wastewaters that contain COD from 500 mg/L to as high as 100,000 mg/L (Orhon. 2009). Generally this treatment process operates at 1-5 g/l mixed liquor suspended solids (MLSS) and has a sludge retention time (SRT) in the range of 8 to 25 days (Stephenson et al. 2000; Cirja et al. 2008).

Many studies describe the difficulties of treating high strength wastewater containing toxic compounds such as; chlorinated phenols, chlorinated aromatic hydrocarbons (Table 2-3). Jin et al. (2010) carried out a study treating pesticide wastewater using a pressurized activated sludge process with medium concentrations of COD (2500-5000 mg/L) (Table 2-3). In this, the traditional activated sludge process was modified to create a pressurised aerated tank to overcome oxygen mass transfer. It was reported that when using a pressure at 0.30 MPa and an aeration time of 6h, the concentration of COD was reduced from 500-5000 mg/L to 230-370 mg/L, removing between 85-92.5% COD (Table 2-3). Mcallister et al. 1993 and Quan et al. 2004 used a laboratory scale continuous flow activated sludge unit, consisting of a partitioned aeration tank with a hydraulic retention time (HRT) of 4.9h and solid retention time (SRT) of 35h (Mcallister et al. 1993) and HRT of 8h (Quan et al, 2004). In the study of Mcallister et al. (1993) more than 84% of the recalcitrant pesticides (2,4-D, MCPA, PCOC, 2,4-DCP and 2,4,5-TCP) were removed from landfill leachate. Quan et al. (2004) acclimatised the activated sludge in a conventional activated sludge system with and without bioaugmentation over a period of 6 months to determine the removal percentage of 2,4-DCP. Results showed that the non bioaugumented system removed 60.2% 2,4-DCP whereas bioaugmentation system removed up to 95.4% 2,4-DCP (Quan et al. 2004) (Table 2-3). McAllister et al. (1993) did recommend a physical adsorption process such as an activated carbon (AC) as a post treatment process for the removal of residual total organic carbon (TOC) and toxicity from the activated sludge prior to discharge to the environment.

[redacted] Trickling filters

Trickling filters are continuous fixed bed reactors that operate under aerobic conditions. Wastewater is trickled over the packing media allowing the wastewater to percolate through the media colonised by micro-organisms. Over time, the biofilm degrades the organic compounds in the wastewater.

Studies using trickling filters to degrade pesticides in wastewater are very limited (Butler & Boltz, 2014; Simsek, Kasi, Ohm, Blonigen, & Khan, 2013). Although literature shows trickling filters can be utilised to treat high strength wastewaters of 10,000 mg/L COD with removal efficiency between 60-70% (Kornaros & Lyberatos, 2006), there is no information about pesticide treatment in this processes (Table 2-3). The only exception is the pesticide production wastewater treated at a UK full scale STW (Table 2-3). The area of active filter bed was 84000 m^2 and the volume is 168,000 m^3. The hydraulic loading and

BOD rates were 0.42 m^3/m^2.day and 0.015 kg BOD/m^3.day, respectively. The produced effluent had an average COD and BOD of 60.31 mg/L and 7.68 mg/L, respectively, presenting percentage removals of 64.8 % for COD and 89.5% for BOD. The removals of pollutants were often above 75%, except for 2,4-DB with 36.6% removal and MCPB with 43.5%. Prior to discharge the effluent was further diluted with the STW effluent at an estimated 4-fold dilution (Soares, 2015).

Table 2-3. Overview of biological processes used to treat pesticide production wastewater.

Process	Scale	Type of wastewater	Influent	Effluent	% Removal	Comments	Reference
Activated sludge	Laboratory scale	Landfill leachate	2,4-D:1420 mg/l MCPA:2020 mg/l PCOC: 520 mg/l 2,4-DCP: 50 mg/l MCPB: 4 mg/l	PCOC: 26 mg/l, MCPA & MCPB: 21 mg/L Chlorophenols (2,4-D, 2,4-DCP): 235 mg/L	PCOC: 95% MCPA & MCPB: 99.5% Chlorophenol: 84%	Reduced toxicity by 76%, Flow rate -177ml/h, HRT - 4.9 h, SRT- 34.9 h	Mcallister et al. 1993
Activated sludge with bioaugmentation	Laboratory scale	Synthetic pesticide wastewater	2,4-DCP: 24.7-28.3 mg/l	2,4-DCP: <15 mg/l	60.2% (no bioaug.) 95.4% (bioaug.)	HRT - 8 h; pH 7-7.8; 24h. Acclimatised sludge over a period of 6 months by synthetically adding 2,4-DCP	Quan et al. 2004
Pressurized activated sludge	Laboratory scale	Real pesticide wastewater (China)	COD: 2500-5000 mg/L	COD: 350-450 mg/L	85%-92.5% COD in 6 h	Aeration time 6 h Pressure 0.30 MPa Operation temp 25°C	Jin et al. 2010
Activated sludge	Laboratory scale	Municipal wastewater	MCPP: <0.36 µg/L	<LOD - 0.18µg/L	0% - 38%	pH 6.6-7.8 HRT 7-10 h	Bernhard et al. 2006
Trickling filters	Pilot scale	Dye production wastewater	COD: up to 36,000 mg/L	COD: 5000 mg/L	60% - 70%	pH 5.5 -8.0. Operation cycle 24 h Aeration phase 23 h HRT 15 h Flow rate 500 m^3/h	Kornaros & Lyberatos 2006
Trickling filters	Full scale	Real pesticide wastewater (full scale WWTP, UK)	Influent to trickling filters (in µg/L) 2,4-D: 220.39 2,4-DB: 13.67 2,4-DCP 2500.00 2,4-DP: 20.14 2,4,6-TCP: 87.40 MCPA: 155.18 MCPB: 17.89 MCPP: 64.24	(in µg/L) 2,4-D: 34.98 2,4-DB: 8.67 2,4-DCP 403.60 2,4-DP: 4.39 2,4,6-TCP: 20.47 MCPA: 29.14 MCPB: 10.11 MCPP: 11.33	2,4-D: 84% 2,4-DB: 37% 2,4-DCP: 84% 2,4-DP: 78% 2,4,6-TCP: 77% MCPA: 81% MCPB: 43% MCPP: 82%	Average flow: 442 m^3/day 28 units at 20 m width, 150 m length, 2 m depth Active filter bed area: 84000 m^2 & volume 168000 m^3 Hydraulic loading rate: 0.42 m^3/m^2 BOD loading rate: 0.015 kg BOD/m^3	Soares, 2015

[redacted] Anaerobic treatment

Existing studies have reported the removal of chlorophenol pesticides including 2,4-DCP using anaerobic pathways (Maltseva et al., 1996). Anaerobic breakdown usually takes place by reductive dehalogenation in which chlorine atoms are substituted by hydrogen atoms. Dehalogenation continues into lesser-chlorinated phenols and further degraded into methane and carbon dioxide. More specifically, for 2,4-DCP the compound is mineralised via phenol, 4-hydroxybenzoic acid and benzoic acid (Figure 2-2) (Arora & Bae, 2014).

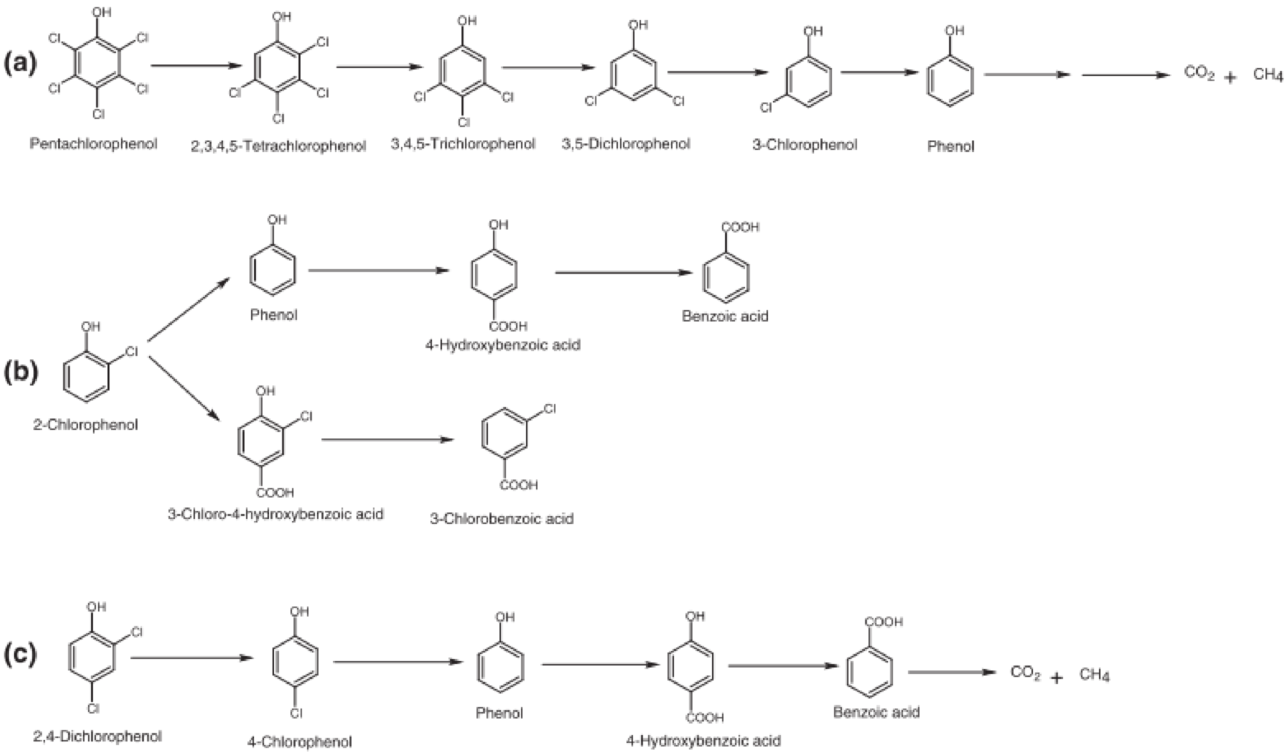


Figure 2-2. Anaerobic degradation of chlorophenols including 2,4-DCP (C) (Arora & Bae, 2014).

2.3.3 Physical treatment

Physical treatments such as filtration, coagulation and adsorption and more specifically granular activated carbon (GAC) processes are exceptionally good at removing solids, specific pollutants with high octanol/water coefficient (Log K_{ow}) and high adsorption-desorption coefficient (K_d), usually indicating good adsorption. From the physical chemical properties of pesticide production wastewater charactisation discussed earlier (Table 2-2) the compounds 2,4-D,

2,4-DB, 2,4-DCP 2,4-DP, 2,4,6-TCP, PCOC, MCPA, MCPB and MCPP show potential to be removed via adsorption. Adsorption is often used for removal of recalcitrant pollutants due to its capacity, efficiency and applicability on a large scale and low costs (Daneshvar, 2007; Sotelo et al., 2002; Salman & Hameed, 2010). The most effective and most frequently used adsorbent for organic removal in wastewater is activated carbon (Aksu & Kabasakal, 2004).

[redacted] Activated Carbon

Activated carbon (AC) has been used extensively over the last 40 years to remove a wide range of persistent compounds from wastewater. With advantages such as its resistance to shock loads and efficient odour and colour removal and due to its highly developed surface properties such as porosity, surface area and surface chemistry (Bonvin et al., 2016; Foo & Hameed, 2010; Knopp et al., 2016; Mailler et al., 2016; Martinez et al, 2006). Activated carbon is produced from carbonaceous sources such as coconuts, peat, coal and wood. The raw materials are activated by physical modification and thermal decomposition in a controlled temperature furnace. Once sufficiently burnt, the ash is activated using chemicals such as calcium chloride or zinc chloride. These chemicals create the pores inside each individual ash particle giving the final activated carbon product a large surface area per unit volume and a network of interlinking sub microscopic pores where adsorption will take place (Kim et al. 2008; Chemviron Carbon, 2016).

The physical adsorption process works by attracting the pollutants to stick onto the walls of the carbon. The adsorption mechanism happens in three stages. Firstly the pollutant adheres to the exterior surface of the activated particle due to the attractive forces. The pollutants continue to travel through the surface pores and travel deeper inside the AC, where the attractive forces are the strongest. This process continues to attract more pollutants until full capacity is reached. When this occurs the AC will need to be replaced with new AC or regenerated. Factors that affect the adsorption capacity are composition of the wastewater, pollutants being adsorbed, pH, temperature and contact time (Baup et al, 2000; Amirault et al, 2003; Areerachakul et al. 2007).

AC can be applied in a number of forms; the two most popular types are GAC and powder activated carbon (PAC). GAC particles have higher initial costs when compared to PAC, due to the size of the particles being large enough to be recovered and regenerated when the activated carbon has reached capacity. GAC is regenerated using thermal reactivation, which is an expensive process due to the high-energy costs. Even with GAC having higher initial costs and regeneration costs, from an economical perspective it has a greater adsorption capacity when comparing adsorption of 2,4-D against PAC and other AC media (Table 2-4). From literature, GAC is more likely to be used due the disadvantages of PAC mentioned (Foo & Hameed 2010; Water, 2016; Martinez et al, 2006). PAC has a much lower initial cost as the particles are smaller in size and cannot be reused. Disadvantages of using PAC are clogging up and damaging expensive machinery if not retained in specific tanks or columns and the need to keep replacing and buying PAC as this cannot be re-used (Chemviron Carbon, 2016).

Table 2-4 shows that GAC, more specifically Filtrasorb 400 (a commercial GAC), is a more versatile product capable to removing range of different pesticides when compared to PAC. Maximum adsorption capacity of GAC for pesticides reached up to 516.8 mg/g whilst maximum adsorption capacity for PAC reached 333.3 mg/g, however this is dependent on the type pesticides been adsorbed. When comparing the adsorption capacity for 2,4-D, with GAC, PAC and date stones, the maximum adsorption capacity was 411.1 mg/g, 333.3 mg/g and 238.1 mg/g, respectively (Table 2-4). Filtrasorb 400 was able to remove more pesticides per gram of carbon used (Hameed, Salman, & Ahmad, 2009; Kim et al., 2008; J. Sotelo, 2002; J. L. Sotelo et al., 2002) (Table 2-4).

Aksu & Kabaskal, (2005) carried out batch studies comparing laboratory scale PAC treatment in 2,4-D in synthetic wastewater (Table 2-4). Aksu & Kabaskal, (2005) utilized PAC of 0.1 g in 100 ml solutions at 2,4-D concentrations of 106.0, 204.1, 416.8 and 628.6 mg/L and shaken for a period of 2 days at a temperature of 25^{o}C. The results showed removal levels of 91.9%, 81.0%, 64.8% and 48.8%, respectively.

When pesticide concentrations are higher in the influent wastewater it often leads to lower removal efficiencies as the AC reaches its capacity in a shorter time. Also when treating real wastewater there will be competition for the GAC adsorption pores due to the real wastewater containing other contaminants such as other organic matter. This organic matter interferes with pesticide adsorption by been absorbed and reduces the GAC capacity, leading to lower removal yields (Alrhmoun et al., 2014).

Table 2-4. Overview of pesticide absorption capacities for various types activated carbon.

Process	Scale	Type of wastewater	Influent	Effluent	% Removal	Comments	Reference
Filtrasorb 400 (GAC)	Laboratory scale	Synthetic wastewater	2,4-D: 0.45 mol/m^3 MCPP: 0.45 mol/m^3 Chlorophenoxyacetic acid: 0.45 mol/m^3	2,4-D MCPP Chlorophenoxyacetic acid		Batch tests: AC 0.001 – 0.25 g in 200 ml synthetic solution. Max adsorption capacity: 411.13, 389.20 and 516.85 mg/g Pesticide concentrations kept a constant 0.45 mol/m^3	Kim et al. 2008
AC – Tire granules	Laboratory scale	Synthetic wastewater	Methoxychlor: 12 mg/L Atrazine: 12 mg/L Methyl Parathion: 12 mg/L	Methoxychlor: <1.2 mg/L Atrazine: <2.4 mg/L Methyl Parathion: <3.5 mg/L	Methoxychlor: 91% Atrazine: 82% Methyl Parathion: 71%	Column studies Particle size 200-250 μm Flow rate: 1.5 ml/min	Gupta et al. 2011
Filtrasorb 400 (GAC)	Laboratory scale	Synthetic wastewater	Lindane: 10 mg/L Alachlor: 10 mg/L			Batch tests: 3 days Particle Size: 0.84-1 mm Max adsorption capacity: Lindane: 181.00 mg/g, Alachlor: 151 mg/g	Sotelo et al. 2002
Charcoal based (PAC)	Laboratory scale	Synthetic wastewater	2,4-D: 106-628 mg/L	2,4-D: 97- 307 mg/L	2,4-D: 91.9-48.8%	Batch tests, PAC 0.1 g in 100 ml 2,4-D solution at 25ºC Max adsorption capacity: 333.30	Aksu & Kabasakal 2005
AC - Date stones	Laboratory scale	Synthetic wastewater	2,4-D: 100 mg/L	2,4-D: 30 mg/L	2,4-D: 70%	Batch tests Particle Size: 2-3 mm AC 0.2 g in 250 ml solution Period of 9 hours Max adsorption capacity: 238.10	Hameed et al. 2009

2.3.4 Chemical treatment - advanced oxidation processes (AOPs)

Over recent decades, the number of studies on UV-based AOPs such as UV/H_2O_2, O_3, UV/O_3, photocatalysis (UV/TiO_2) or the Fenton process (H_2O_2/Fe) is rapidly increasing due to their ability to remove persistent pollutants (Badawy et al., 2006; Barbusiński & Filipek, 2001; Irmak et al., 2004, 2006; Kowalska et al., 2004; Mokrini et al., 1997). These new technologies have been acknowledged as extremely efficient at eliminating a wide range of organic compounds in wastewater including pesticides. Existing studies showed AOPs having the ability to degrade toxic pesticide compounds to less toxic compounds and even accomplished full mineralisation (Cheng et al., 2015; Lafi & Al-Qodah, 2006; Meijers et al. 1995). As a result more wastewater treatment plants are incorporating treatments using AOPs (Badawy et al., 2006; Vincenzo Naddeo, 2013).

Advanced oxidation processes use catalysts (titanium dioxide, iron ions, or other transition metals), oxidants (O_3 or H_2O_2) and radiation (solar light, UV light or ultrasounds) either solely or combined. The most recognised and commercially available processes that are utilised for treating wastewater are ozonation (O_3), ultra violet light with ozone (UV/O_3) and ultra violet light with hydrogen peroxide (UV/H_2O_2) (Suty, De Traversay, & Cost, 2004). Photocatalysis describes accelerated photoreaction in the presence of a catalyst that is activated by light (the photocatalyst). The absorption of light causes the chemicals to change chemical states as molecules transfer electrons leading to the breakdown of pollutants into smaller compounds that are usually more easily degradable.

AOPs generate very powerful, non-selective hydroxyl radicals (HO•) that are short lived (Comninellis et al., 2008; García-Montaño et al., 2006). These hydroxyl radicals degrade the organic compounds in the wastewater by oxidizing them. Organic compounds with second rate constants compound-radical between the order of 10^6-10^9 1/M.s or higher, are likely to be oxidised by AOPs (Lafi & Al-Qodah, 2006). Rates of degradation are different for every compound and depend on the formation of oxidant species such as the radical scavengers in the wastewater as well as the hydroxyl radical. To overcome this and attain full mineralisation usually high amounts of chemicals are used. However this is impractical and exceptionally expensive especially when utilized on large scales (Wu and Linden, 2008).

Table 2-5. Overview of the AOP processes used for removal of pesticide from wastewater.

Processes	Scale	Type of wastewater	Influent	Effluent	% Removal	Comments	Reference
UV/TiO_2	Laboratory scale	Synthetic wastewater	PCOC: N/A	PCOC: N/A	51.4%	pH 2.7 Reactor volume 130 ml 0.5 g/L TiO_2 Max radiation 365 nm	Irmak et al. 2004
UV/H_2O_2	Pilot scale	Real pesticide production wastewater (Poland)	2,4-D: 65 μg/L	2,4-D: <0.1 μg/L	95%	150 W medium pressure mercury vapour lamp. Irradiated for 40 minutes. UV/H_2O_2	Kowalska et al. 2004

						Reactor volume 100L H_2O_2 dose 0.8 v/v	
Fenton	Laboratory scale	Synthetic wastewater	Fenitrothion: 50 mg/L Diazinion: 50 mg/L Profenofos: 50 mg/L	Fenitrothion: 22.95 mg/L Diazinion: 43.55 mg/L Profenofos: 24.85 mg/L	Fenitrothion: 54.1% Diazinion: 12.9% Profenofos: 50.3%	Reactor volume 0.85L Optimal pH 3 Removal concentrations after 90 minutes	Badawy et al. 2006
Photo-Fenton	Laboratory scale	Synthetic wastewater	Fenitrothion: 50 mg/L Diazinion: 50 mg/L Profenofos: 50 mg/L	Fenitrothion: 6.55 mg/L Diazinion: 21.65 mg/L Profenofos: 5.15 mg/L	Fenitrothion: 86.9% Diazinion: 56.7% Profenofos: 89.7%	Reactor volume 0.85L UV Lamp 100-280 nm Optimal pH 3 Removal concentrations after 30 minutes	Badawy et al. 2006
UV/O_3	Laboratory scale	Synthetic wastewater	Deltamethrin: 100 mg/L COD: 6500 mg/L	Deltamethrin : <10 mg/L COD: 5200 mg/L	Deltamethrin: 90-100% COD: 20%	pH 4 or above Ozonation 3.5 h 4200 mg ozone entered the oxidation reactor. UV emitted at 253 nm Ozone flow rate 240 mg/h/L	Lafi & Al-Qodah 2006
Ozonation	Laboratory scale	Synthetic wastewater	2,4-D, 2,4-DP, MCPA, and MCPP 0.9- 6.4 µg/L		2,4-D: >80% 2,4-DP: 86% MCPA: 100% MCPP: 100%		Meijers et al. 1995
Ozonation/ H_2O_2	Laboratory scale	Synthetic wastewater	2,4-D and 2,4-DP 0.9- 6.4 µg/L Atrazine: N/A		2,4-D: >95% 2,4-DP:>96% Atrazine: 100%	H_2O_2/O_3 >0.5g/g Temp 5-25ºC Atrazine pH 7, 10 mins – 100% degradation Atrazine pH 8 , 1 min – 100% degradation	Meijers et al. 1995
Fenton	Laboratory scale	Mixture of pesticide production wastewater and landfill leachate (Poland)	Organochlorine pesticides : Up to 377.1 µg/dm^3	Organochlorine pesticides: N/A	90 - 100% removed	Completely degraded achieved only with H_2O_2 concentration of 5 g/dm^3. Optimum ratio of ferrous ion to H_2O_2 was between 1:2 and 1:3 with an optimum pH between 3- 3.5	Barbusiński & Filipek 2001

[redacted] Ozonation

Ozone is an unstable gas that readily degrades from O_3 to O_2 (Equation 2-1) to produce a highly reactive free radical that is stronger and less selective than chemical oxidants. Consequently ozone can successfully react and breakdown a wide range of organic pollutants and water (Equation 2-2 and 2-3). The mechanism for this process starts with the ozone generation. This is achieved by running an electric current through the air, which charges the molecules and converts O_2 to O_3. Ozone is introduced into contact tanks where it is dissolved in water. It can react directly with the pollutants or with water, yielding hydroxyl radicals. These free radicals are extremely unstable and short lived therefore they need to be generated in-situ. Due to the short reaction times ozonation allows a vast amount of wastewater to be treated in high throughput processes. Ozonation is a powerful oxidation technique that has long been used to treat water for odour management, disinfection and colour removal in the water treatment industry. Since then studies have been carried out and have proven ozonation is effective at degrading a number of recalcitrant organic pollutants including pesticides 2,4-D, 2,4-DP, MCPA, and MCPP in wastewater (Meijers et al., 1995; Ikehata & Gamal El-Din., 2005; Alvares et al., 2001).

$$3O_2 + \text{ENERGY} \rightarrow 2O_3 \quad \textbf{(Equation 2-1)}$$

$$2O_3 + \text{POLLUTANT} \rightarrow \text{BY-PRODUCT} \quad \textbf{(Equation 2-2)}$$

$$O_3 + H_2O \rightarrow OH\bullet \quad \textbf{(Equation 2-3)}$$

Meijers et al. (1995) utilised this process on the above compounds at concentrations between 0.9-6.4 µg/L, the removal rates were between 80-100%. The study then continues looking at the effects of ozone combined with hydrogen peroxide for 2,4-D and 2,4-DP at the same concentrations between 0.9-6.4 µg/L the removal rates were >95% and >96%, respectively. These results indicate that when combining ozone with hydrogen peroxide significantly higher removal rates can be achieved (Table 2-5) (Meijers et al. 1995).

[redacted] Fenton process

The Fenton process is one of the most effective methods for oxidising organic pollutants in industrial wastewater. The Fenton reagent is constituted by a mixture of hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}). The ferrous iron (Fe^{++}) initiates and catalyses the decomposition of H_2O_2, thus generating hydroxyl radicals (OH•) (Equation 2-4). In this reaction ferrous iron is oxidised to ferric iron, which then reacts again with hydrogen peroxide, yielding more radicals (Equation 2-5). These two reactions constitute the iron redox cycle, where iron acts as a catalyst. The generation of hydroxyl radicals comprises of a complex sequence of reactions (Equations 2-6 to 2-9). They can react with pollutants, oxidising and transforming them into by-products; they can react with other radicals; or with other ions/compounds in water (inefficient Equations). Hydrogen peroxide can also act as a hydroxyl scavenger as well as an initiator during these reactions (Equations 2-7 to 2-9) (Pignatello, Oliveros, & MacKay, 2006).

Fe (photo) redox cycle: $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\bullet$ **(Equation 2-4)**

Fenton: $Fe^{3+} + H_2O_2 \rightarrow OH\bullet + HOO\bullet + Fe^{2+}$ **(Equation 2-5)**

$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^-$ **(Equation 2-6)**

$OH\bullet + H_2O_2 \rightarrow H_2O + OOH\bullet$ **(Equation 2-7)**

$OOH\bullet + Fe^{3+} \rightarrow O2 + Fe^{2+} + H^+$ **(Equation 2-8)**

$\bullet OH + RH \rightarrow R\bullet + H_2O \rightarrow$ products **(Equation 2-9)**

The efficiency of Fenton's oxidation process depends on hydrogen peroxide and ferrous ion concentrations, pH and time of the reaction. For Fenton process to work successfully, the pH should be between 2.5 - 4.0 (Oller et al., 2011). In 2001, Barbusiński & Filipek studied the impact of the Fenton's process on the removal of organochlorine pesticides (concentrations up to 377.1 µg/L) in industrial wastewater. Using a hydrogen peroxide dose of 5 g/L at pH 3.0 - 3.5 all pesticides were completely removed (Barbusiński & Filipek, 2001) (Table 2-5).

In 2006, Badawy et al. studied the effects of removing pesticides from a synthetic solution via Fenton and photo-Fenton treatment processes (Table 2-5). Using a reactor volume of 0.85 L and pH 3 and a 150 W medium pressure mercury lamp (100-280 nm). The results evidently indicate that the most effective method was the photo-Fenton process with higher removal rates between 57-90% in 30 minutes, compared to the Fenton process removal rates between 13-54% in 90 minutes (Badawy et al., 2006).

[redacted] Ultraviolet (UV) photolysis

UV light is a type of electromagnetic radiation with frequencies of around 8×10^{14} to 3×10^{16} cycles per second, known as hertz (Hz), and is categorised into four types: UV-A (near UV) between 315–400 nm; UV-B (middle UV) between 280–315 nm; UV-C (far UV) between 180–280 nm and vacuum (extreme UV) between 10-180 nm. Different UV lamps can be used to treat wastewater: low pressure mercury lamps (LP-UV - wavelength at 253.7 nm) are capable of providing power up to 0.4 kW and medium pressure lamps (MP-UV), can produce UV and visible light in the UV-C range of 180-280 nm and power up to 30 kW (Zhang & Pagilla 2010; Badawy et al. 2006; Giannakis et al. 2015). UV-C range is more commonly utilised when applied in combination with hydrogen peroxide (Vincenzo Naddeo, 2013).

When treating recalcitrant pollutants in wastewater, UV alone is not often used, as it is a slow process and efficient only for compounds absorbing light at the emitted wavelength of the lamp. So UV is commonly combined with hydrogen peroxide or ozone (Table 2-5) (Kowalska et al., 2004; Lafi & Al-Qodah, 2006). Combining either will generate more hydroxyl radicals that will bond and oxidise the pollutants in the wastewater and increase the rate of degradation. Other substances can be added such as catalysts such as titanium dioxide (TiO_2), this also helps to increase the creation of hydroxyl radicals (Irmak et al., 2004; Oller et al., 2011). This treatment process is currently not been used at large scale, but studies have been carried out at bench/pilot scale work which would be easily scalable.

[redacted] Ultraviolet/hydrogen peroxide (UV/H_2O_2)

Treatment processes based on hydrogen peroxide and UV (at 200-280 nm) generate high concentrations of hydroxyl radicals (·OH) (Vincenzo Naddeo, 2013). This process is the most studied AOP and the only one used at large scale. Studies show that UV/H_2O_2 processes are extremely efficient in the removal of wide range recalcitrant compounds including organic pesticides and is currently used for pesticide removal in drinking water (Kowalska et al., 2004).

Kowalska et al. (2004), studied the removal of organic pesticides including 2,4-D in industrial wastewater using UV/H_2O_2 (Table 2-5). In this study, filtration, sedimentation and coagulation were used as pre-treatment stages in order to reduce solids and enhance the pesticide removal efficiency at reduced irradiation, and therefore reduced costs. Kowalska et al. 2004 used an air-sparged hydrocyclone reactor containing 100 L of industrial wastewater, doses of H_2O_2 of 80 mg/L, 40 minutes irradiation time and a 150 W MP-UV. The study showed the removal of 95% 2,4-D (Kowalska et al., 2004). From earlier studies Kowalska et al. 2002 established that the optimum dose of hydrogen peroxide was critical and must be experimentally determined (Kowalska et al. 2002). Findings showed that at low hydrogen peroxide concentrations, the UV radiation instigates the generation of damaged hydroxyl radicals. Whereas at high concentrations of hydrogen peroxide, this acts as a trap to the hydroxyl radicals and compete with pollutants, reducing degradation efficiencies (Equation 2-10) (Kowalska et al., 2004).

$$HO\cdot + H2O2 = HOO\cdot + H2O \quad \textbf{(Equation 2-10)}$$

[redacted] Ultraviolet/ozone (UV/O_3)

Treatment processes based on ultraviolet/ozone have a very high oxidation potential (2.8 eV). This high oxidation potential is greater than molecular ozone on its own, which means it can attack inorganic and organic molecules non selectively at very high reaction rates (Ikehata & Gamal El-Din, 2005). For this process to work efficiently certain parameters need to be carefully controlled such as, ozone dosage, UV irradiation level and pH. A high dissolved ozone rate must be sustained with an effective transfer of ozone gas into the wastewater. This can be achieved by using a pressurised injection mix UV/ozone reactor to produce microbubbles that constantly top up the ozone gas. This type of reactor maintains and significantly improves the solubility of the gas allowing enhanced UV radiation. Furthermore, this set-up results in increased pH levels which forces the ozone to produce additional hydroxyl radicals, thus increasing the oxidation rate (Ikehata & Gamal El-Din, 2005). In 2006, Lafi & Al-Qodah used UV/O_3 to remove pesticides and COD from aqueous solutions (Table 2-6). In this study, the aqueous solutions (100 mg/L Deltamethrin and 6500 mg/L COD) were adjusted to pH 4, UV was emitted at 253 nm and an ozonation period of 3.5 h with an ozone flow rate of 240 mg/L.h was used. The results showed pesticide removal between 90% and 100% over a period of 210 minutes. COD levels reduced by 20% but only at a pH of 4 or above (Lafi & Al-Qodah, 2006).

[redacted] Ozone/hydrogen peroxide (O_3/H_2O_2)

This combination of ozone/hydrogen peroxide is generally used in wastewater with very resistant pollutants or in very high concentrations that would result in the consumption of large amounts of oxidant. Ozone generation can be expensive and therefore combining with H_2O_2 makes the process more feasible (Mokrini et al., 1997). During the reaction between ozone and H_2O_2, hydroxyl radicals are formed (Equation 2-11). The stoichiometric ratio for the production of hydroxyl radicals between H_2O_2 and ozone is 0.35 g/g. For optimal formation of hydroxyl radicals the ratios are generally between 0.5-1 g/g (Ijpelaar, Groenendijk, Hopman, & Kruithof, 2002).

$$2O_3 + H_2O_2 \rightarrow 2OH\bullet + 3O_2 \quad \textbf{(Equation 2-11)}$$

Meijers et al, (1995) investigated the degradation of pesticides by ozonation and advanced oxidation. They found that efficiency of hydroxyl radical formation via ozone and H_2O_2 process is determined by pH of the water and is relatively independent of the H_2O_2 dose ($H_2O_2/O3 > 0.5$ g/g) and temperature (5°C-25°C). Results showed that increasing the pH changes the oxidation mechanism from molecular ozone pathway (2.1 eV) to a radical oxidation potential (2.8 eV), therefore significantly increasing the rate of the reaction. For example, in the case of atrazine, at pH 7 the reaction took 10 minutes to degrade whereas at pH 8 the reaction was completed within 1 minute (Meijers et al., 1995).

A full scale UV/ozone/peroxide treatment system for removing volatile organic compounds (VOCs) and chlorinated compounds was built and run for four years. The system was able to removed 94.6% VOCs. After 4 years the system was modified and improved to a UV/ H_2O_2 system. This system was able to achieve removals of 99.95% VOCs and 100% PCBs with initial influent concentration around 0.3 µg/L (Clarin et al., 2000).

2.3.5 Hybrid treatment processes

[redacted] Membrane bioreactor (MBR)

Combining activated sludge with other biological/physical/chemical treatments processes enhances treatment efficiency. Activated sludge can be coupled with a membrane. A membrane bioreactor (MBR) is a hybrid treatment system that utilises an activated sludge process system with a membrane filtration in which the final settler is substituted by ultra-filtration or micro-filtration membranes, which retains all suspended solids therefore only allowing the clean effluent to pass through (Cirja et al., 2008). The membrane can be placed in various ways such as completely immersed or partially immersed in the activated sludge reactor. Submerged MBRs are currently replacing cross-flow MBRs due to being more energy efficient (Haandel and Lubbe, 2011). There are several membrane types available but for retaining particles between 1-5 nm nanofiltration (NF) membranes are indicated, as these that can be used to retain dissolved particles. To retain particles sized between 5-100 nm ultrafiltration (UF) membranes are indicated and these can also remove virus and smaller bacteria. For particle sizes between 100-1000 nm, i.e., suspended particles microfiltration (MF) membranes can be used. When treating high strength industrial wastewater shock loads might occur, for this reason MF are more commonly used allowing the retention of suspended solids, but not dissolved particles such as soluble microbial products, that would lead to membrane clogging and decrease the membrane life (Mutamim et al. 2013). There are many advantages to using MBRs rather than conventional activated sludge systems including:

- small-foot print (usually 30 - 50%) due to higher biomass concentrations. Conventional ASP generally operates at 1-5 g/l MLSS, whilst the MBR operates significantly higher MLSS between 8-25 g/l, in some cases even higher concentrations allowing for higher reaction rates and consequently smaller foot-prints (Cirja et al., 2008);
- high effluent quality. MBR treatment eliminates all suspended solids and pathogens in the effluent, whilst standard activated sludge systems will require an additional tertiary processes to achieve the same effluent quality (Haandel et al. 2011);
- simple process operation. MBRs are simple to operate,
- low sludge production. The long sludge retention times (SRT) in MBRs i.e., SRT for MBR are between 25-150 days compared to conventional treatment processes typically between 8-25 days (Stephenson et al. 2000; Göbel et al. 2007; Radjenović et al. 2009; Cirja et al. 2008) allows for sludge hydrolysis, reducing its production;
- enhanced pollutant removal. The sludge retained in the MBR can adsorb pollutants. It was found that the longer the SRT in the MBR, the more chance of microbial degradation of the pollutants (Spring et al, 2007).

MBR systems were originally used in treating domestic wastewater on various scales, (Lim et al, 2004) but over the last decades it has been developed and used for industrial wastewater treatment, including pesticides and pharmaceuticals. These wastewaters contain a wide spread of pollutants that are either slowly biodegradable or not biodegradable at all. Studies show that biodegradation rate is mostly affected by the adaptability of the microorganisms and the nutrients they get from the wastewater (Navaratna, Shu, & Jegatheesan, 2016; Phan et al., 2015; Tauseef, Abbasi, & Abbasi, 2013).

Yang et al. (2006) and Bernhard et al. (2006) carried out studies comparing laboratory scale MBR and activated sludge treatment in biodegradation of persistent organic pollutants (POPs) in pesticide wastewater (Table 2-6). Bernhard et al. (2006) utilized a submerged MBR prototype with three chlorinated polyethylene membrane plates with a surface area of 0.1 m^2 and pore size of 0.4 µm. The pH ranged between 6.6- 7.8 and the MBR had an HRT of 7 - 10h. The results showed that recalcitrant pollutants were completely removed. However MCPP removal percentage was between 36 - 64% (Bernhard et al., 2006; Yang et al., 2006).

Sahar et al. (2011) compared the differences in removal efficiencies between MBR and CAS for hydrophilic compounds trimethoprim and sulphamethoxazole, both have K_{ow} values less than 1.0. Results showed that the MBR was more efficient due to hydrophilic compounds depending on biodegradation removal rather than been adsorbed on the biomass like hydrophobic compounds, providing the microorganisms can adapt with the compounds in the wastewater and by providing longer contact time MBR usually are able to biodegrade compounds better than conventional activated sludge (Sahar et al, 2011).

[redacted] Aerobic-anaerobic process

Literature shows limited research on using an anaerobic-aerobic process on pesticide wastewater at full scale. Shawaqfeh. (2010) studied the removal of pesticides from a synthetic wastewater using combined anaerobic-aerobic biological treatment. In this study, two small identical glass cylinders (height: 25 cm, diameter: 10 cm) were used for aerobic (22°C and HRT of 24h) and anaerobic conditions (30°C and HRT of 12h), respectively, and packed with 0.5 cm polyethylene terephthalate (PET) plastic beads with a diameter of 0.5 cm. The study showed the removal of 25 mg/L triadimenol ($C_{14}H_{18}ClN_3O_2$, chlorinated polycyclic aromatic hydrocarbon) by 96% after an acclimation period of 230 days in the anaerobic reactor and 172 days in the aerobic reactor (Shawaqfeh, 2010). The process increased biomass concentrations and the HRT was reduced from 12h to 8h (anaerobic) and 24h to 16h (aerobic) when compared to the individual processes. The results showed a removal of 98% in

COD, showing that this hybrid process could treat pesticide wastewater (Shawaqfeh, 2010).

[redacted] GAC – biological process (pre-treatment or post-treatment)

Oh and Tuovinen (1994), studied the biodegradation of the phenoxy pesticides MCPP and 2, 4-D in fixed film column reactors with GAC. Operating conditions were: 180 mL continuous flow reactor, a temperature at 22°C and an aeration rate of 200 ml/min. GAC was used as a biomass support matrix to grow the microbial biofilm. Results showed that 2,4–D was completely degraded in 4 days whilst MCPP efficiently removal was 88% at 7 days (Tuovinen & Oh, 1994).

A full scale pesticide manufacturing company in Australia has developed a combined process that includes trickling filters, activated carbon and sequence batch reactors. There is limited data about the process or the results obtained. The trickling filters were used as a pre-treatment of an activated carbon system to remove the high COD levels before entering sequence batch reactors (GHD, 2015). Other studies also show that biological process can be used prior to activated carbon to increase its efficiency and reduce costs. Using a biological process prior to activated carbon removes most of the competing organic matter and other easily biodegradable compounds in the wastewater allowing the activated carbon to adsorb the target pesticides and reduce frequency of regeneration (Foo & Hameed, 2010; Kaminski et al., 2014; Salman & Hameed, 2010).

A more recent study showed a laboratory scale MBR combined with GAC (post treatment) in the removal of trace organic contaminants in synthetic wastewater. The MBR was seeded with AS from another MBR had been in continuous operation for over 3 years. The MBR operating conditions were: 24 hours HRT, a temperature of 20°C, a dissolved oxygen concentration of 3 mg/L and a pH in the range of 7.2-7.5. The GAC column operating conditions were: 7.5 g GAC and a flow rate of 2.4 ml/min (7 min EBCT). Results showed removal levels after the MBR were below 40% (fenoprop, naproxen, diclofenac, ketoprofen and carbamazepine), after GAC treatment removal efficiencies reached >98% (Nguyen et al., 2012). Other studies show utilizing GAC as a post treatment is a viable option for eliminating trace organic from biological treated wastewater (Alrhmoun et al., 2014; Dickenson & Drewes, 2010; Grover et al., 2011; Nguyen et al., 2012).

[redacted] GAC - AOPs

More recent studies show the combination of GAC with chemical processes such as AOPs. Areerachakul et al. (2007) combined GAC fixed bed adsorption with a continuous photocatalysis system to remove pesticides from wastewater. In this study, a combination of columns were used with different bed depths (5, 10, 15 cm) packed with GAC and operated at empty bed contact times for several weeks. The removal of metsulfuron-methyl reached 35, 55 and 65% respectively. When using a continuous photocatalysis system using TiO_2 the results showed removal rates between 40-60%. However when combining both processes GAC followed by photocatalysis system using TiO_2, the results showed removal rates of over 90% with a retention time of less than 10 minutes (Areerachakul et al, 2007). TiO_2 is a technology under development and there is limited research on the process been scaled up. Gu et al, (2010), confirms the success of hybrid systems where utilizing GAC with supported TiO_2 and photocatalysis to degrade 2, 4-D is very efficient with 100% removal within 90 minutes (Gu et al., 2010a) (Table 2-6).

Other studies report the utilisation of ozonation as a pre-treatment prior to GAC, this is so all remaining organic compounds and by-products of degradation can be completely removed before discharged (Lenntech, 2016). Other studies have combined activated sludge with ozonation treating real wastewater at pilot scale (Table 2-6). Existing literature supports pre-treatment rather than post treatment due to the positive impact on removing the remaining pollutants in the following biological treatment, such as activated sludge. However if treating strongly polluted wastewater, high dosing would be required, and consequently usually ozonation is deemed economically unfavourable due to the high cost implications. Therefore if using ozonation on a large scale with highly polluted wastewater post ozonation would be the preferable option or other treatment options would be used (Li et al, 2010; Lafi & Al-Qodah 2006).

[redacted] Biological- AOPs

Existing literature indicates promising results using AOPs as a pre-treatment for degrading pesticides into more readily biodegradable intermediates which can then be fully treated by a biological treatment process (Lafi & Al-Qodah, 2006; Parra et al., 2000).

Research shows an increase in studies for combining Fenton process with other processes such as biological treatments, UV and photo-catalysis, to reduce costs, enhance pesticide removal and reduce toxicity (Table 2-6) (Chen, Sun, &

Chung, 2007; Giannakis et al., 2015; Moreira et al., 2012; Vilar et al., 2012; Zapata et al., 2010). Treating pesticide wastewater using a combined biological and solar driven Fenton process is a highly efficient process. Using UV lamps are also efficient but would give very different results because of the emitting spectrum. Moreira et al. (2012) combined an immobilised biomass reactor (IBR) as pre-treatment biological process step using a flat bottom tank (50 L) and IBR tank (45 L) at pH 6.5-7.5 and an air flow rate of 20 L/min with several different AOPs including Fenton, UV, TiO_2/UV (with and without acidification) and the processes were repeated with the addition of hydrogen peroxide. The Fenton process was controlled at pH 2.6-2.9, 140 mg Fe^{2+}/L and H_2O_2 200- 500 mg/L. TiO_2 concentrations were added up to 200 mg/L. They found that TiO_2/H_2O_2/UV with acidification was the most successful, not only did the process remove the highest pesticide removal efficiency of over 90% including recalcitrant pesticides 2,4-D and MCPA the rate of reaction was much quicker; 18 out of the 19 pesticides were degraded within 28KJuv/L. However their research indicated that no pesticides were degraded after the IBR (Table 2-6) (Moreira et al., 2012).

Kastanek & Maleterova (2007) used Fenton process as a pre-treatment combined with an aerobic activated sludge biological treatment to completely degrade 4- chlorophenol in wastewater (Table 2-6). 4- chlorophenol is from the same chemical group as 2,4-DCP and have very similar characteristics and this was chosen as model compound due to the limited biodegradability. The aim of this study was to utilise the Fenton process to modify the chemical structure of 4-chlorophenol with the purpose of generating biodegradable intermediates which would enhance the biodegradability. The Fenton process conditions were 200 mL samples at pH 3 at a temperature of 40°C, with doses of Fe^{2+} - 0.1- 14 g and H_2O_2 – 17 mL and stirred for 170 minutes. After the pH was adjusted to 6.5 and activated sludge was added. The samples were kept at 25°C in the dark overnight. The results showed up to 80% 4-chlorophenol removal. By using a combination of Fenton reagent and a biological treatment process to remove recalcitrant pesticides offers economical and feasible advantages (Kastanek, Maleterova, & Kastanek, 2007). Combining with a biological process reduces costs and the amount of chemicals required (Lafi & Al-Qodah, 2006; Parra et al., 2000).

[redacted] Biological- Electrochemical

Fontmorin et al. (2013) combined an electrochemical system with a biological treatment to study the removal 2,4-D in real pesticide wastewater at laboratory scale. In this study an electrochemical flow cell was used for pre-treatment using a graphite felt as an electrode (48 mm diameter and 12 mm width) and was kept at a constant 1.6 V/SCE and a flow rate of 1 ml/min. Biological experiments were carried out in 250 mL conical flasks containing 100 mL activated sludge and stirred at 250 rpm at 30°C. The study showed the removal of 30 mg/L 2,4-D by 66% in 2 days, 79% within 7 days and 85% within 21 days (Fontmorin et al., 2013).

[redacted] AOPs - Ultrasonic

Ozonation has been studied in combination with chemicals oxidants such as potassium permanganate, chlorine dioxide, and hydrogen peroxide. However molecular ozone has a higher oxidation potential of 2.07 V than conventional chemical oxidants listed above (Ikehata & Gamal El-Din, 2005). In 2011, Xiong et al, studied pre-treatment of heterocyclic pesticide wastewater combining ultrasound and ozone processes. In this study, 100 mL pesticide wastewater was treated with ultrasound (power 300 W at 20-60 kHz) and dosage of O_3 of 454.8 mg/L.min. The results showed significantly enhanced biodegradability and decreased levels of toxicity (from 11% to 52%). BOD_5/COD ratio increased from 0.03 to 0.55. It was found that the process was more favourable in alkaline conditions (pH 9) and the COD removal was improved when the ultrasound frequency was low (20 kHz) (Xion et al., 2011).

[redacted] AOPs – AOPs

Studies show that coupling UV/H_2O_2 with the photo Fenton process is also a remarkably efficient treatment process. Badawy et al. (2006) used this process and compared it with the Fenton process for the removal of organo-phosphorus pesticides in wastewater. The aim was to remove 3 different compounds, fenitrothion, diazinion and profenofos. Using a reactor volume of 0.85 L and pH 3, for the photo-Fenton process a 150 W medium pressure mercury lamp was used between 100-280 nm. The results showed that Fenton treatment removed 54.1%, 12.9% and 50.3%, respectively after 90 minutes, whereas combining UV/H_2O_2 with the Fenton treatment the results were 86.9%, 56.7% and 89.7%, respectively after 30 minutes. UV/H_2O_2 with the Fenton treatment is found to be much more efficient giving higher percentage removal and at a much quicker rate. The reason for these results can be explained looking at Equations 2-12. Equation 2-4 shows the Fenton process reaction, one ferrous ion (Fe^{2+}) generates one hydroxyl radical (OH•) therefore ferrous ion can potentially be a limiting factor and affect the rate of hydroxyl radicals been produced therefore decrease the rate of degradation. Whereas in the UV/H_2O_2 with the Fenton treatment process (Equation 2-12) the UV radiation contributes by photolysis of Fe^{3+} complex ions and the hydrogen peroxide to generate hydroxyl radicals. The hydrogen peroxide also reduces Fe^{2+} from the photolysis of Fe^{3+} which in turn is oxidised by hydrogen peroxide and produces further hydroxyl radicals therefore speeds up the oxidisation of the organic compounds (Badawy et al., 2006).

$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + OH\bullet + H^+ \quad \textbf{(Equation 2-12)}$$

Table 2-6. Overview of the combination of biological, physical and chemical processes (hybrid processes) used for removal of pesticide from wastewater.

Processes	**Scale**	**Type of wastewater**	**Influent**	**Effluent**	**% Removal**	**Comments**	**Reference**
MBR	Laboratory scale	Domestic wastewater	MCPP: Unknown	MCPP: <LOD - 0.10µg/L	38% - 64%	HRT 7-10 h Submerged MBR prototype with three membrane plates each with a surface area of 0.1 m^2, mesh width of 0.4 µm. Membrane was chlorinated polyethylene	Bernhard et al. 2006
MBR	Pilot scale	Real wastewater	Sulfamethoxazole: N/A	Sulfamethoxazole: N/A	80%	HRT 13 h SRT 16 d, 30 d, 60-80 d Flow rate 1.3 m^3/h	Göbel et al. 2007
Aerobic/Anaerobic Biological Process	Laboratory scale	Synthetic wastewater	Triadimeno: 25 mg/L	Complete degradation	96%+	Aerobic: Acclimation 172 days HRT 24 h Operating temp 22ºC Anerobic: Acclimation 230 days HRT 12 h Operating temp 30ºC	Shawaqfeh. 2010
Activated Sludge electrochemical flow cell	Laboratory scale	Synthetic wastewater	2,4-D: 30 mg/l (can be up to 500 mg/L)	2,4-D: 10.2 mg/L	66% in 2 days, 79% within 7 days, 85% within 21 days	Porous electrode at a constant 1.6 V/SCE Flow rate of 1 mL/min. Stirred at 250 rpm at 30°. Inoculated with 0.5 g L-1 of activated sludge. pH 7	Fontmorin et al. 2013

Photo-Fenton	Laboratory scale	Synthetic wastewater	Fenitrothion: 50 mg/L Diazinion: 50 mg/L Profenofos: 50 mg/L	Fenitrothion: 6.55 mg/L Diazinion: 21.65 mg/L Profenofos: 5.15 mg/L	Fenitrothion: 86.9% Diazinion: 56.7% Profenofos : 50 mg/L 89.7%	Reactor volume 0.85L UV Lamp 100-280 nm Optimal pH 3 Removal concentrations after 30 minutes	Badawy et al. 2006
Ozonation/ H_2O_2	Laboratory scale	Synthetic wastewater	2,4-D & 2,4-DP: 0.9- 6.4 µg/L	2,4-D & 2,4-DP: N/A	2,4-D: > 95% 2,4-DP: >96%	H_2O_2/O_3 >0.5g/g Temp 5-25ºC Atrazine pH 7 – 10 mins – 100% degradation Atrazine pH 8 – 1 min – 100% degradation	Meijers et al. 1995
Fenton/ Microwave electrodeless ultraviolet (MWEUV)	Laboratory scale	Real pesticide production wastewater (China)	COD: 33,700 mg/L Dimethoate, Triazophos, and Malathion: N/A	COD: 9300 mg/L Dimethoate, Triazophos, and Malathion: N/A	COD: >85% Dimethoate, Triazophos, and Malathion: 100%	Optimal conditions Fe^{2+} 0.8 mmol/L H_2O_2 100 mmol/L, pH 5. 120 mins Temp 25ºC	Cheng et al. 2015
IBR/Photo-Fenton/IBR	Pilot scale	Domestic wastewater	2,4-D: 33,552-43,645 ug/l, MCPA:29,052-38,752 ug/L	2,4-D: <200 ug/L MCPA: <100 ug/L	2,4-D: >99% MCPA: >99%	Biological reactor volume 80 L Flow rate 250 L/h pH 6.5-7.5 Fenton Fe^{2+}/ 140 mg/L every 15 mins pH adjusted to 2.6-2.9 200-500 mg/L H_2O_2	Vilar et al. 2012
Immobilised biomass reactor (IBR)/UV/Fenton, IBR)/UV/TiO_2/ H_2O_2 and IBR/UV/TiO_2	Pilot scale	Wastewater resulting from phyto-pharma. plastic containers washing	2,4-D & MCPA : 25,000 ug/L	2,4-D & MCPA : up to 2,500 ug/L	2,4-D & MCPA : >90%	Biological system flat bottom tank 50 L and IBR 45 L tank. pH 6.5-7.5 Air flow 20 L/min After 5-8 Kjuv/L. No pesticides were degraded after the IBR. IBR. Fenton – pH 2.6-2.9 140 mg Fe^{2+}/L H_2O_2 200- 500 mg/L IBR-UV/TiO_2 – up to 200 mg/L	Moreira et al. 2012
UV/O_3/bioreactor	Laboratory scale	Synthetic wastewater	COD: 6500 mg/L	COD: <325 mg/L	COD: >95%	pH 4 or above. Ozonation was 3.5 hours. During this oxidation time, 4200mg ozone entered the oxidation reactor.	Lafi & Al-Qodah 2006

						Bioreactor 6 L tank Flow rate 200 L/h	
TiO_2 and Photo-Fenton/IBR	Pilot scale	Synthetic wastewater	Methomyl: 50 mg/L Dimethoate: 50 mg/L Oxamyl: 50 mg/L Cymoxanil: 50 mg/L Pyrimethanil: 50 mg/L	Methomyl: 5 mg/L Dimethoate: 5 mg/L Oxamyl: 5 mg/L Cymoxanil: 5 mg/L Pyrimethanil: 5 mg/L	Methomyl: >90% Dimethoate: >90% Oxamyl: >90% Cymoxanil: >90% Pyrimethanil: >90%	TiO_2 - 35L solar pilot plant tank TiO_2 .- 200 mg/L Photo-Fenton- 75L solar pilot plant tank pH 2.7-2.9 Fe^{2+} 20 mg/l and 55 mg/l H_2O_2 – 200-500 mg/L IBR - 60L – neutralisation tank, 25 L conditioner tank, 35 L IBR tank pH 6.5-7.5 Flow rate 1.6 L/min	Oller et al. 2007
Photo-Fenton/IBR	Pilot scale	Synthetic wastewater	Pesticides: 500 mg/L	Pesticides: 0 mg/L	100% removed	Photo-Fenton batch mode pH 2.7-2.9 20 mg/L $Fe^{2+.}$ IBR - 1230 L tank pH 7-7.5. Batch or continuous Flow 120L/h, HRT 20h	Zapata et al. 2010
Fenton/Activated Sludge	Laboratory scale	Synthetic wastewater	4- chlorophenol: 301-313 mg/L	4-chlorophenol:90-131 mg/L	4-chlorophenol: <80% removed in 42 days	Sample 200 ml Adjusted to pH 3 Fe^{2+} - 0.1- 14g Temp 40ºC H_2O_2 – 17 mL (Fenton process 170 mins long) Adjusted to pH 6.5 Temp 25ºC and activated sludge added. Samples kept in dark	Kastanek & Maleterova, 2007
Activated sludge, Moving Bed Bioreactor, Coagulation-Flocculation - UV, UV/ H_2O_2, Fenton, Photo-Fenton	Laboratory scale	Domestic wastewater	MCPP: 235 ng/L (Activated sludge), MCPP:20 ng/L (Moving Bed Bioreactor), MCPP: 26 ng/L (Coagulation-Flocculation)	MCPP: <58.75 ng/L (Activated sludge), MCPP:<5 ng/L (Moving Bed Bioreactor), MCPP: <6.5 ng/L	100% removed by UV/ H_2O_2. >25% removed by Fenton/photo-Fenton	Micropollutants removed; Efficiency increased in following order: Coagulation-Flocculation (20%), Activated sludge (25%), Moving Bed Bioreactor (40%). AOPs UV/ H_2O_2most efficient. UV-C – 254 nm (10-30 mins) H_2O_2 – 25 mg/L	Giannakis et al. 2015

						Fe^{2+} - 5 mg/L HRT – 4 h SRT – 2 d	
GAC - TiO_2/UV	Pilot scale	Petro-chemical wastewater	2,4 –DCP: 22 mg/L	2,4 –DCP: 0 mg/L	2,4 –DCP: 100%	100% removal with 9 g/l Ti–GAC with 90 mins. Reactor tank – flow rate 32 L/h Contact time 30 mins Air flow rate 5 L/min Ti-GAC 112g	Gu et al., 2010
Activated Sludge electrochemical flow cell	Laboratory scale	Real wastewater	2,4-D: 30-500 mg/l	2,4-D: <330 mg/L	2,4-D : 66% in 2 days, 79% within 7 days, 85% within 21 days	Porous electrode at a constant 1.6 V/SCE Flow rate of 1 ml/min 100 mL of medium, stirred at 250 rpm, kept at 30°C Inoculated with 0.5 g L-1 of activated sludge. pH 7	Fontmorin et al. 2013
Fenton/SBRs	Laboratory scale	Synthetic wastewater	2,4-D and MCPA: 180 mg/L	2,4-D and MCPA: 18 mg/L	90%	Fenton pH 3 H_2O_2/Fe^{2+} - 10:1 ratio SBRs - 3L SBR, Air flow 9L/min. Temp 30ºC, 200 rpm and pH 7. Sequences of 8 h as follows: anoxic filling (1 h) aerated reaction (5.5 h) settling (1 h) and draw (0.5 h) HRT - 12 h	Sanchis et al. 2013
UV/TiO_2 - biological	Laboratory scale	Synthetic wastewater	2,4-D: 800 mg/L	2,4-D: 70-280 mg/L	2,4-D : Photo-catalytic treatment - Up to 60% removed in 21 hrs. Bio treatment >90% removed between 20-24 hrs	TiO_2 - 1 g/l UV – 256 nm pH 7 Biological- 50 mL sample 5% sludge – mixed overnight Temp – 30ºC 200 RPM	Samir et al. 2015

2.4 Discussion

Pesticide production wastewater is a high strength complex wastewater that requires bespoke treatment before it can meet industrial consent to discharge to sewer or meets consent to discharge direct to watercourse (rivers/streams). The Environmental Quality Standards (EQS) set the discharge limits for this specific wastewater, which are; 7.1 mg/L (2,4-D), 73 mg/L (2,4-DCP), 219 mg/L (MCPP) and 70.2 mg/L (MCPA).

A large proportion of the pollutants in pesticide production wastewater such as lactic acid, glycolic acid, 2-ethylhexanol, n-butanol, i-butanol, isopropyl acetate are easily biodegradable and can easily treated using biological processes. These pollutants are likely to be responsible for providing the highest pollutant load in the pesticide production wastewater measured as BOD. Hence it is typically recommended that a biological process is included on the possible options to treat the wastewater. After extensive review of the existing literature regarding treatment of pesticide rich wastewater (Tables 2-3, 2-3, 2-5 and 2-6) it is clear that activated sludge can successfully achieve pesticide removal between 0-99.5% for the following compounds 2,4-D, 2,4-DP, 2,4-DCP, PCOC, MCPA, MCPB and MCPP in concentrations from 0.00036 - 2020 mg/L at laboratory scale (Bernhard et al., 2006; Mcallister et al., 1993). At a full scale STW where trickling filters have been used to treat pesticides 2,4-D, 2,4-DB 2,4-DP, 2,4-DCP, 2,4,6-TCP, PCOC, MCPA, MCPB and MCPP, pesticide removals have been observed in the range of 37-84% with initial concentration in the range of 14-2500 µg/L (Soares, 2015). Suggesting that pesticide production wastewater should be able to be treated by biological processes such as activated sludge, or more effectively even, by using MBR systems. MBR has the potential to improve the treatment of pesticide wastewater as it can reach higher effluent qualities and most importantly it has increased of resilience to toxic loads as a results more studies are been reported. These MBR systems were originally used in treating domestic wastewater at various scales but over the last decades MBRs have been developed and used for industrial wastewater treatment including pesticides and pharmaceuticals (Lim et al, 2004).

From existing literature it has been shown that 2,4-D, 2,4-DP, MCPA, PCOC and MCPP can be removed by various AOPs in synthetic and real pesticide wastewater at laboratory and pilot scale with pesticide removals in the range of 50-100% (Badawy et al., 2006; Barbusiński, 2005; Barbusiński & Filipek, 2001; Ijpelaar et al., 2002; Kowalska et al., 2004; Lafi & Al-Qodah, 2006; Suty et al., 2004). However there are no reports on full-scale applications and there are very limited reports on commercial processes. On the other side physical treatments such as activated carbon appear to be a treatment option which has been applied by different industries. Looking at the field of pesticides treatment, it has been proven that GAC more specifically F-400 can remove recalcitrant pollutants including 2,4-D and MCPP at levels of 100% and 88%, respectively. However when looking to treat pesticide wastewater that contains high concentrations (mg/L) it has been seen that higher concentrations in the influent wastewater often leads to lower removal efficiencies as the AC reaches its capacity in a shorter time. Also when treating real wastewater there will be competition for the GAC adsorption pores due to the real wastewater containing other contaminants such as other organic matter. This organic matter interferes with pesticide adsorption by being absorbed and reduces the GAC capacity, leading to lower removal yields (Alrhmoun et al., 2014).

On the other hand even if the average pesticide production removals of 99% are achieved in the biological, chemical and physical processes, this would still result in effluent qualities with total pesticide concentration (sum of all 2,4-D; 2,4-DP; 2,4-DB; 2,4-DCP; 2,4,6-TCP; PCOC; MCPA; MCPB AND MCPP) in the order between 1-5 mg/L and compliance with the WFD EQS would be a risk of been breached. The majority of existing literature focusses on pesticide wastewater at low pesticide concentrations in the range of µg/L and usually in mixtures of one to four different pesticides; the more common pesticides 2,4-D, 2,4-DCP, MCPA and PCOC (Fontmorin et al., 2013; Irmak et al., 2004; Kowalska et al., 2004; Mcallister et al., 1993; Quan et al., 2004).

Therefore an application of a hybrid system utilising biological treatment with pre/post treatment chemical or physical would be necessary to ensure that these pesticides are removed to the required limits prior to being discharged. Research suggests that using a hybrid processes combining biological processes with physical and chemical processes are extremely successful in treating pesticide wastewater and some studies have proven to achieve complete mineralisation. AOPs can be combined with a biological process as a pre or post treatment stage. Many studies utilise activated sludge process with UV/H_2O_2, Fenton, photo-Fenton, O_3, UV/O_3, UV/O_3/H_2O_2. Studies show that utilising a hybrid process increases the removal of pesticides (Badawy et al., 2006; Chen et al., 2007; Cheng et al., 2015; Comninellis et al., 2008; Ebrahiem et al., 2013; Giannakis et al., 2015; Gu et al.,2010a, 2010b; Ikehata et al., 2004, 2006, 2008; IKastanek et al.,2007; Mokrini et al., 1997; Moreira et al., 2012; Oller et al.,2011; Vincenzo, 2013). On the down side, most of the processes described to date on the combination of AOPs with a biological process have been proven at lab-scale or pilot-scale. Applications at full-scale are very scarce and important parameters, such as process design, operation and costs would require further trials at a demonstration scale.

The vast majority of studies focus on low pesticide concentrations in synthetic and real wastewater, but the pesticide production wastewater in this study has a very high strength wastewater (mg/L) that contained many toxic pollutants. The characterisation of the pesticides physical and chemical properties, existing literature and current commercial treatments show that these chlorinated herbicides (2,4-D, 2,4-DB, 2,4-DCP 2,4-DP, 2,4,6-TCP, PCOC, MCPA, MCPB and MCPP) can be removed by biological processes but potentially not to the EQS discharge limits. The pesticides have a hydrophobic nature and good adsorption capacities (Log Kd above 1.5 and Log K_{ow} over 2.5) therefore using a physical adsorption treatment such as GAC would further remove the pollutants in the wastewater (up to 99.9%) and provide a cheaper and more reliable alternative treatment option to AOPs, (Ahmed et al., 2017) as the fate of the pollutants is unclear due to the K_{oH} values been around 10^9 1/M.s. Also there is very limited data on full scale processes. Existing literature shows GAC has been commercially applied by different industries (GHD, 2015) and studies show that using GAC as a post-treatment as opposed to pre-treatment has more advantages such as; regeneration becomes less frequent, removal rates increase and reaction time is the order of minutes. Further to this, GAC has the ability to resist shock loads and can improve odour and colour removal (Bonvin et al., 2016; Foo & Hameed, 2010; Knopp et al., 2016). Therefore combining GAC as a post-treatment with a biological process such as an MBR would have more advantages by reducing operation and set up costs and produce a high quality effluent that would comply with the EQS discharge limits.

2.5 Conclusion

Most studies found in literature focused on synthetic solutions, synthetic wastewater, at lab-scale or pilot-scale. Although these studies can provide information on the removal mechanisms and provide a comparison between process efficiency, they have limited practical applicability. The process that has been more widely used to treat high strength wastewaters rich in recalcitrant compounds at full-scale, is the combination of biological/GAC and GAC/biological processes. The pesticide production wastewater contains a variety of compounds, that can be removed by 80-90% using biological processes (such as MBR) and GAC has been shown to selectively remove the pesticides, potentially creating a high quality effluent. Nevertheless, in order to assert processes design, efficiencies or costs, it is crucial to evaluate these processes experimentally.

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▌High performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC-MS) method development for quantifying pesticides in wastewater

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3.1 Abstract

New high performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC-MS) analytical methods were developed for quantification of 9 pesticides found in wastewater originated from an industrial facility dealing with the formulation of pesticides. These pesticides included: 2,4-dichlorphenoxy acetic acid (2,4-D); 4-(2,4-dichlorphenox) propionic acid (2,4-DP); 4-(2,4-dichlorophenox) butyric acid (2,4-DB); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy) butyric acid (MCPB) and 2-(4-chloro-2-methylphenoxy) propionic acid (MCPP). The HPLC method used a LC18 based column (Fortis Cyano) with a mobile phase of 70:30 consisting of de-ionised water: acetonitrile + 0.4% acetic acid (70:30) and the UV detector set at 280 nm. A good separation of the 9 compounds was achieved after 25 minutes with limit of detections (LOD) between 0.22 mg/L and 0.61 mg/L. Previous to the GC-MS analysis, the wastewater samples were concentrated using solid phase extraction (SPE) with methyl-tert-butyl ether (MTBE) followed by derivatisation using trimethylphenylammonium hydroxide (TMPH). The compounds were successfully quantified on a Rtx-5MS fused silica column (30 m x 0.25 mm x 0.25 µm) with LODs in the range of 0.5-1.0 mg/L.

3.2 Introduction

Determination of acidic pesticides: 2,4-dichlorphenoxy acetic acid (2,4-D); 4-(2,4-dichlorphenox) propionic acid (2,4-DP); 4-(2,4-dichlorophenox) butyric acid (2,4-DB); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy) butyric acid (MCPB) and 2-(4-chloro-2-methylphenoxy) propionic acid (MCPP) in complex wastewater requires an application of a selective and sensitive analytical techniques that have the ability to separate and quantify the various compounds, for instance chromatography (Rompa et al., 2005). Existing literature shows high performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC-MS) to be the most common techniques utilised to quantify organic chemicals including pesticides such as 2,4-D, 2,4-DCP, MCPA and PCOC (Mcallister et al., 1993; Irmak et al., 2004; Kowalska et al., 2004; Quan et al., 2004; Fontmorin et al., 2013). The GC-MS offers low quantification levels for pesticides, in the range of µg/L, but it requires sample preparation such as solid phase extraction (SPE) or liquid-liquid extraction (LLE) (Rompa et al., 2005). As a result, GC-MS is a rather expensive option and requires well-trained technical staff. On the other side, HPLC can only quantify concentration levels in the mg/L range. Advantages from using HPLC include reduced or no sample extraction procedure, reducing errors, timescales and complexity (Irmak et al., 2004; Quan et al., 2004).

There is limited literature on methods for the quantification of complex mixtures pesticides in wastewater samples, including the 9 phenoxy acids and dichloro acids pesticide present in the pesticide production wastewater: 2,4-D; 2,4-DP; 2,4,-DB, 2,4-DCP; 2,4,6-TCP; PCOC, MCPA, MCPB and MCPP. The US Environmental Protection Agency (EPA) “Chlorinated herbicides by GC” (Method 8151A) requires methylation or pentafluorbenzylation derivatisation in order to successfully quantify chlorinated herbicides via GC-MS (US.EPA, 1996). However this is a time consuming method that requires a number of different solvents with larger volumes (17-120 ml per sample) and requires large sample volumes (2 L) (US.EPA, 1996). Rompa et al. (2005) describes the use of a much simpler and less time consuming method where samples are cleaned up and concentrated through SPE and evaporated to 1 ml before spiked with trimethylphenylammonium hydroxide (TMPH) and injected into the GC-MS. The SPE requires only small amounts of organic solvents. However, this method only considered 3 (MCPP, MCPA and 2,4-D) of the 9 key pesticides found in the pesticide production wastewater.

Similarly, methods for analysis of pesticides have been developed for HPLC (Quan et al., 2004b; Irmak et al., 2006; Radjenović et al., 2009). The Fortis technologies presented a Cyano column able to separate 2,4-D; 2,4-DP; 2,4,-DB, 2,4-DCP; PCOC, MCPA, MCPB and MCPP, to good resolutions but it this did not include 2,4,6-TCP.

This study focused on the development of HPLC and GC-MS methods for quantification of 9 pesticides in a real pesticide production wastewater with very high complexity.

3.3 Materials and Methods

3.3.1 Chemical/Regents

Chemicals 2,4-D (99+%), 2,4-DCP (99%), 2,4-DP (98%), 2,4,6-TCP (98%) and PCOC (97%), 2,3,4,5-tetrachlorophenol (2000 µg/ml), TMPH (0.5M) and 2,4-DCAA (100 µg/ml) were purchased from Fisher Scientific (UK), 2,4-DB was purchased from VWR (UK) and MCPA (100%), MCPB (100%) and MCPP (100%) were purchased from Sigma-Aldrich (Germany). All solvents were HPLC grade and ultra-pure deionised water was obtained from Milli-Q (purelab, Olga).

3.3.2 HPLC methods

The HPLC used was a Shimadzu DGU-20A5 (Shimadzu, Japan) HPLC equipped with a UV-visible detector (series SPD-20A). The method development involved testing a number of columns and mobile phases according the different methods numbered below:

Method 1- The column test was a LC8 250 mm x 4.5 mm, 5µm column (Phenomenex, UK) with a corresponding 2 cm cartridge guard column (Phenomenex, UK). All compounds were analysed according to the following parameters: the mobile phase was made up from two components; A – 0.025 M phosphoric acid and B – acetonitrile with a gradient program of 0 minutes 20% (B), 50 minutes 90% (B) and 55 minutes 10% (B), a flow rate of 1 ml/min, a temperature of 20°C, an injection volume of 50 µl, the wavelength of the UV detector was 280 nm and analysis run for 60 minutes. The column was allowed to re-establish for 5 minutes before analysing the next sample.

Method 2 – was the same as Method 1, but the mobile phase was adjusted to 0 minutes 20% (B), 6 minutes 28% (B), 10 minutes 28% (B), 30 minutes 90% (B) and 60 minutes 20% (B).

Method 3 - was the same as Method 2 but the gradient program was changed to a isocratic method with B tested at 5% and 20%.

Method 4 - The columns were LC18 Luna phenyl-hexyl 250 mm x 4.5 mm, 5µm column (Phenomenex, UK) and Eclipse 250 mm x 4.6 mm, 5µm column (Phenomenex, UK). The mobile phase was made up from two components; A – 0.025 M phosphoric acid and B – acetonitrile with a gradient program of 0 minutes 10% (B), 30 minutes 90% (B) and 55 minutes 10% (B), a flow rate of 1 ml/min, a temperature of 20°C, an injection volume of 50 µl, the wavelength of the UV detector was 280 nm and analysis run for 30 minutes. The column was allowed to re-establish for 5 minutes before analysing the next sample. All compounds had retention times within 30 minutes and were able to separate 8 of the 9 compounds.

Method 5 - A Fortis Cyano column 250 mm x 4.6 mm, 5µm (Chromex Scientific, UK) with a corresponding 2 cm cartridge guard column (Chromex Scientific, UK) was used. The mobile phase was made up from two components; A – deionised water and B – acetonitrile with 0.2% acetic acid. An isocratic program was used to separate the analytes. The parameters were 80:20 (A:B) mobile phase, a flow rate of 0.2 and 1 ml/min, a temperature of 20°C, an injection volume of 50 µl, the wavelength of the UV detector was 280 nm and analysis run for 60 minutes. Then the column was allowed to re-establish for 5 minutes before analysing the next sample.

Method 6 – was the same as Method 5 but the mobile phase was adjusted to 70:30 and 60:40; A – de-ionised water and B – acetonitrile with 0.2% acetic acid. Temperature was also adjusted from 20°C to 25 °C and 30°C.

Method 7 – was the same as method 5, but the mobile phase H_2O:acetonitrile changed with concentrations of 0.2% to 0.3% and 0.4% acetic acid, at a flow of 1 ml/min with the isocratic programme 70:30 for 25 min and at 280 nm UV detection.

3.3.3 GC-MS method

[redacted] Sample extraction

The GC-MS extraction method based on a pervious application by Rompa et al., (2005) was developed. Solid phase extraction (SPE) was used to extract the samples. The method development involved testing a number of cartridges according to the different methods numbered below:

Method 1- The cartridge test was a C18 500 mg (Waters, UK). All tests were carried out in triplicates. The SPE cartridges were conditioned with methyl-tert-butyl ether (MTBE) (1x3 ml), methanol (2x3 ml) followed by acidified deionised water pH 3 (1x3 ml) prior to analysis. During the extraction process the cartridges were not allowed to dry out during conditioning and sample percolation. Cartridges were spiked with synthetic pesticide solution. Once the sample had passed through the cartridge, the cartridge was rinsed with 5 mL of acidified water before being dried using a gentle stream of air (around 45 minutes). The analytes were eluted with MTBE (5 ml); dried under a gentle stream of nitrogen, 1 ml MTBE was added and vortexed to re-suspend the pesticides before being transferred to a vial and spiked with 0.5 ml TMPH.

Method 2- The cartridge test was a C18 500 mg (Waters, UK). All tests were carried out in triplicates. The SPE cartridges were conditioned with methyl-tert-butyl ether (MTBE) (1x3 ml), methanol (2x3 ml) followed by acidified deionised water pH 3 (1x3 ml) prior to analysis. During the extraction process the cartridges were not allowed to dry out during conditioning and sample percolation. Cartridges were spiked with synthetic pesticide solution. Once the sample had passed through the cartridge, the cartridge was rinsed with 5 mL of acidified water before being dried using a gentle stream of air (around 45 minutes). The analytes were eluted with MTBE (5 ml); 1 ml MTBE was transferred to a vial and spiked with 0.5 ml TMPH.

Method 3 - was the same as method 1, but with Oasis 500 mg cartridges (Waters, UK).

Method 4 - was the same as method 2, but with Oasis 500 mg cartridges (Waters, UK).

Method 5 - was the same as method 1, but with Sep-Pak Vac 6cc (500 mg) tC18 cartridges (Waters, UK).

[redacted] GC-MS method

The GC-MS method based on a pervious application by Rompa et al., (2005) was developed. The instrument used was an Agilent 6890 GC (Agilent, USA) coupled with an Agilent 5973 mass selective detector (MSD) and an Agilent 6890 series auto sampler. It was equipped with an Rxi HT-5 capillary column (30 m, 0.25 mm I.D., and 0.25 µm film thickness) (Phenomenex, UK) and a split/splitless injection port operating in the splitless mode. Data acquisition was in the SIM (selected ion monitoring) mode for quantitative analysis. In SIM mode, the dwell time of each ion is set to be 100 milliseconds. The injection temperature was 250 °C, splitless mode, carrier gas helium 1 ml/min, with an oven temperature programme 80 °C to 200 °C at 6 °C/minute, 200 °C to 280 °C at 30 °C/minute for 5 minutes. The GC-MS method description for analysis is summarised in Table 3-4. Only ultra-high purity helium (99.999% pure) was used as a carrier gas. A moisture trap, an oxygen trap, and an organic trap was connected in series to the carrier gas line before it enters the column.

3.4 Results and Discussion

3.4.1 HPLC

A systematic approach was put in place to develop the methodology, including testing a number of standard columns and a range of mobile phases. Method 1, 2 and 3 resulted in low peak resolution. For Method 1, the compounds had retention times between 4.4-6.6 minutes for Method 2 it was between 2.9-3.6 minutes, but in both case, the 9 peaks could not be separated. With method 3, good separation was obtained for 6 compounds with retention times between 6-10 minutes, whilst 20% was able to separate 4 peaks in 6-10 minutes, but the 9 peaks could not be separated. Method 4 allowed the separation of 8 of the 9 compounds and the retention times were < 30 minutes. Although this method yielded promising results, the 9 peaks could not be separated. Method 5 was able to separate 6 compounds and an increase in mobile phase flow rate to 1 ml/min, resulted in the separation of 8 compounds. With Method 6, with mobile phase 70:30, 8 peaks were detected within 25 minutes but a mobile phase of 60:40 was only able to separate 4 peaks. Increasing temperature to 25^{o}C and 30 ^{o}C did not have any impact.

The best results were obtained for Method 7, using a Fortis column, with the mobile phase H_2O:acetonitrile with 0.4% acetic acid at a flow of with the isocratic programme 70:30 for 25 min and at 280 nm UV detection (Table 3-1). The retention time for the different chlorinated aromatic herbicides are found in Figures 3-1 and 3-2.

Table 3-1. HPLC method used to detect and quantify 9 phenoxy acids and dichloro acids in pesticide production wastewater

Column	250 mm x 4.6 mm, 5µm with a corresponding 2 cm cartridge guard column (Chromex Scientific, UK)
Mobile phase	A – de-ionised water and B – acetonitrile + 0.4% acetic acid (70:30)
Running time	25 minutes
UV (nm)	280 nm
Flow rate	1 ml/min
Temperature	20°C
Injection volume	50 µl

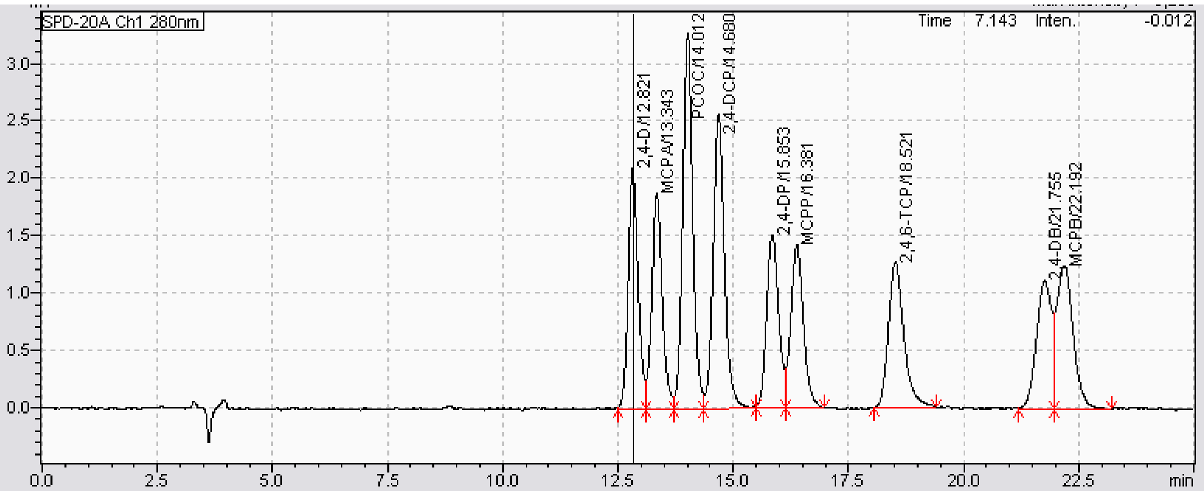

Figure 3-1. Chromatogram of the key pollutants in the synthetic pesticide solution. The retention times were: 2,4-D – 12.7 mins; MCPA – 13.2 mins; PCOC – 13.9 mins; 2,4-DCP – 14.6 mins; 2,4-DP – 15.7 mins; MCPP – 16.3 mins; 2,4,6-TCP – 18.4 mins; 2,4,-DB – 21.7 mins and MCPB – 22.1 mins.

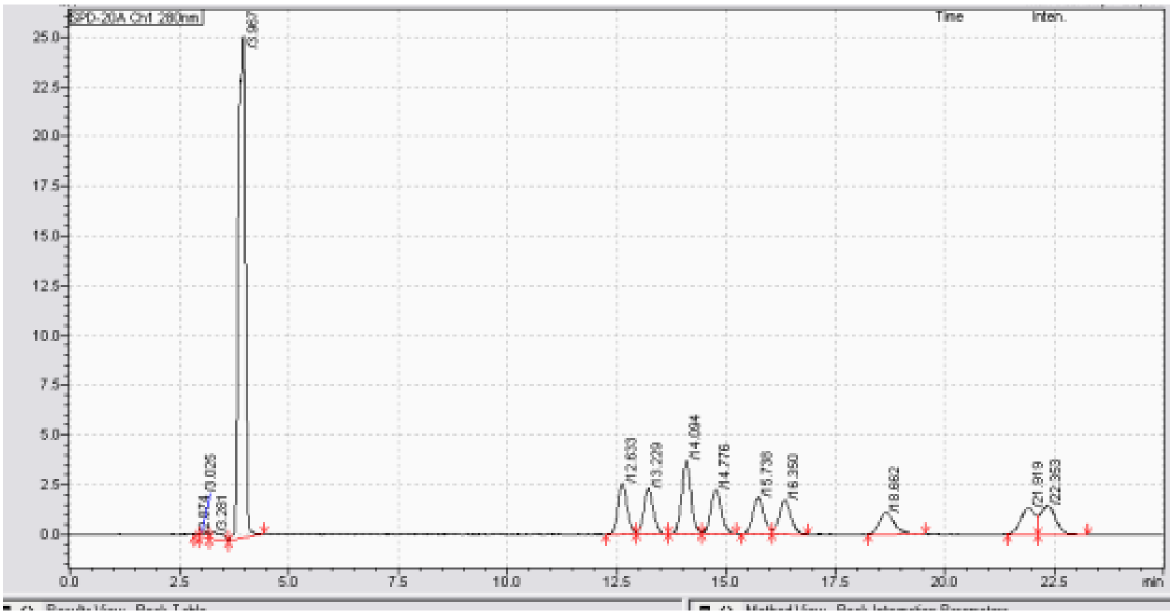

Figure 3-2. Chromatogram of the key pollutants in the pesticide production wastewater. The retention times were: 2,4-D – 12.6 mins; MCPA – 13.2 mins; PCOC – 14.1 mins; 2,4-DCP – 14.7 mins; 2,4-DP – 15.7 mins; MCPP – 16.3 mins; 2,4,6-TCP – 18.6 mins; 2,4,-DB – 21.9 mins and MCPB – 22.4 mins.

The LOD for the individual compounds can be found in Table 3-2. The LOD for the compounds are in the range of 0.22 mg/L and 0.61 mg/L. This was expected of the HPLC as the instrument is not capable of quantifying very low concentrations and agrees with other existing literature (Rompa et al., 2005).

Table 3-2. Limit of detection of the target pesticides for the HPLC method.

Compounds	**LOD (mg/L)**
2,4-D	0.35
MCPA	0.37
PCOC	0.22
2,4-DCP	0.28
2,4-DP	0.45
MCPP	0.61
2,4,6-TCP	0.58
2,4-DB	0.42
MCPB	0.56

3.4.2 GC-MS

A systematic approach was put in place to develop the methodology, including testing a number of SPE cartridges. Method 1, 2, 3 and 4 resulted in loss of peaks. For Method 1, 2, 3 and 4, three of the nine compounds were not present. Results showed loss of pesticides in all four experiments with both cartridges indicating that loss of recovery isn't by evaporation.

The best results were obtained for Method 5, using Sep-Pak Vac 6cc (500 mg) tC18 cartridges (Waters, UK) and the method description (Table 3-3). The retention time for the different chlorinated aromatic herbicides are found in Figures 3-3 and 3-4.

Table 3-3. GC-MS method description used to detect and quantify 9 phenoxy acids and dichloro acids in pesticide production wastewater.

Instrument	Agilent 6890 Series II Gas Chromatograph (GC) with an Agilent 5973MSD and 6890 autosampler
Column	Rxi HT-5 capillary column by Resteck or equivalent (30 m, 0.25 mm I.D., and 0.25 □m film thickness)
Carrier Gas	Helium, ultra-high purity grade (99.999%)
Inlet Temperature	250 °C
Transfer Line (detector) Temperature	320 °C
Oven Temperature Program	80 °C to 200 °C at 6 °C/minute 200 °C to 280 °C at 30 °C/minute for 5 min
Flow Rate	Constant flow at 1 mL/min Linear velocity: 37 cm/s
Injection Volume	1 μL
Split/splitless Mode	Splitless
Total Run Time	28 minutes

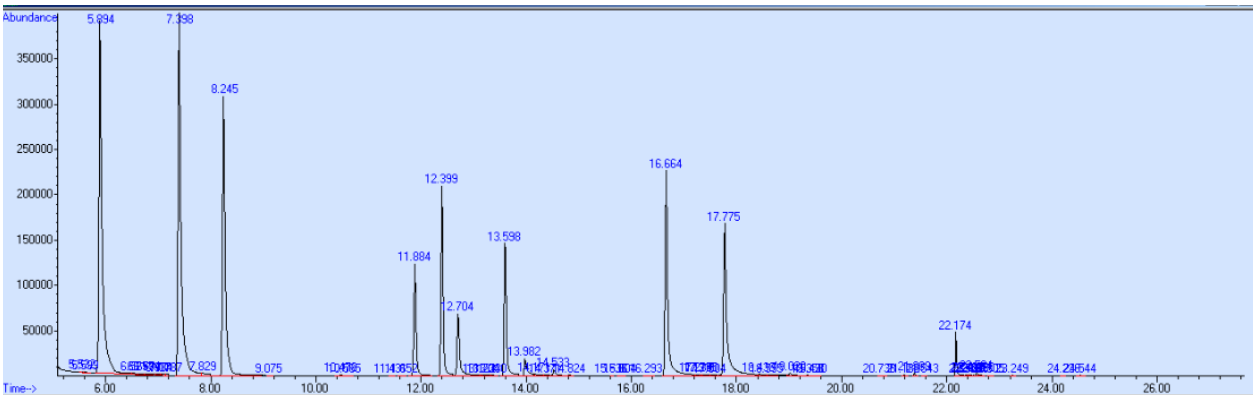

Figure 3-3. Chromatogram of the key pollutants in the synthetic pesticide solution. The retention times were: PCOC – 5.9 mins; 2,4-DCP – 7.4 mins; 2,4,6-TCP – 8.2 mins; 2,4-DCAA (S)– 11.8 mins; MCPP – 12.4 mins; MCPA – 12.7; 2,4-DP – 13.5 mins; 2,4-D – 14.0 mins; 2,3,4,5-Tetrachlorophenol (IS) – 14.5 mins; MCPB – 16.7 mins and 2,4,-DB – 17.7 mins.

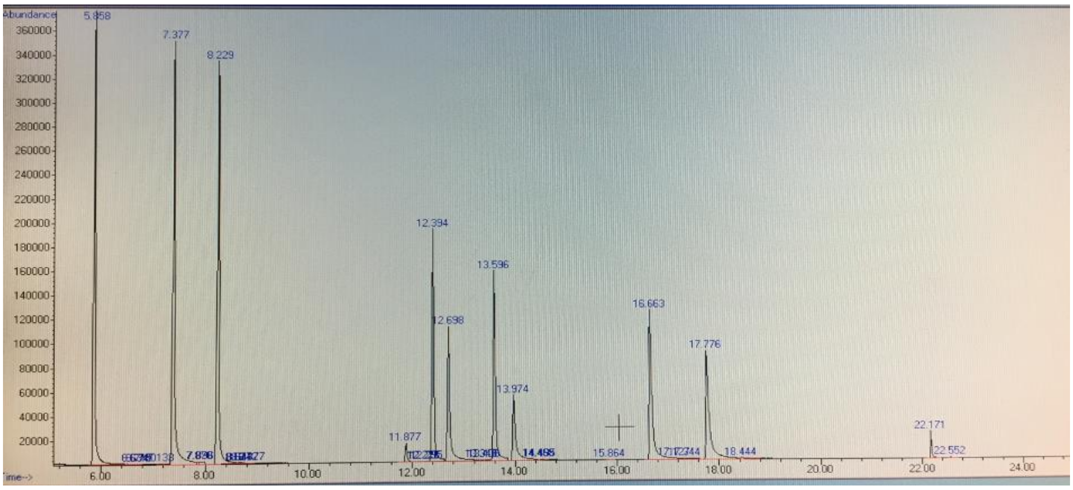

Figure 3-4. Chromatogram of the key pollutants in the pesticide production wastewater. The retention times were: PCOC – 5.9 mins; 2,4-DCP – 7.4 mins; 2,4,6-TCP – 8.3 mins; 2,4-DCAA (S)– 11.8 mins; MCPP – 12.4 mins; MCPA – 12.7; 2,4-DP – 13.6 mins; 2,4-D – 14.0 mins; 2,3,4,5-Tetrachlorophenol (IS) – 14.5 mins; MCPB – 16.7 mins and 2,4,-DB – 17.8 mins

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Table 3-4 shows the extraction recovery of the compounds in synthetic solution. Results show good recoveries for all compounds >75% (except 2,4-D (63%) and 2,4-DB (73%)) suggesting that the method is a successful process. Results for the pesticide production wastewater showed good recoveries, this is seen in the recovery of the surrogate standard (2,4-DCAA) at 79%. Furthermore the results show that the method was good at producing reproducible results as all compound except 2,4-DCP, MCPP and MCPA had standards deviations in the range of 0.05- 1.9. Existing methods such as method 8151A developed by the US EPA discussed earlier accepted recoveries in the range of 70-130% (US.EPA, 1996), whilst other methods where able to achieved recoveries in the range of 60-80% (Rompa et al, 2005). This confirmed that the extraction method used is suitable.

Table 3-4. Recovery of compounds in synthetic pesticide solution and concentrations of compounds and recovery of surrogate standard in pesticide production wastewater using Sep-Pak Vac 6cc (500 mg) tC18 cartridges (Waters, UK).

	Synthetic wastewater		**Pesticide production wastewater**	
Compound	**Mean**	**STDEV**	**Mean (mg/L)**	**STDEV**
PCOC	97%	0.045	37.7	1.8
2,4-DCP	76%	0.151	99.2	5.1
2,4,6-TCP	76%	0.157	2.0	0.2
MCPP	114%	0.112	22.1	2.4
MCPA	99%	0.083	74.4	8.5
2,4-DP	76%	0.035	1.0	0.2
2,4-D	63%	0.023	4.0	1.0
MCPB	92%	0.029	2.4	0.4
2,4-DB	73%	0.026	8.9	1.9
2,4-DCAA (S)	-	-	79%	0.05

*(S) – Surrogate standard

The LOD for the individual compounds can be found in Table 3-5. The LOD for the compounds are in the range of 2.99 and 3.28 µg/L. The LODs were calculated based on the standard deviation of the response (Sy) of the curve and the slope of the calibration curve (S) at levels approximating the LOD according to the formula: LOD = 3.3(Sy/S). A value of 0.001 was assumed as the standard deviation of the response, agreeing with the LODs from Rompa et al. (2005).

Table 3-5. Limit of detection of the target pesticides for the GC-MS method.

Compounds	**LOD (µg/L)**
2,4-D	3.22
MCPA	3.25
PCOC	3.25
2,4-DCP	2.99
2,4-DP	3.25
MCPP	3.26
2,4,6-TCP	3.26
2,4-DB	3.22
MCPB	3.28

A six point calibration curve was obtained by running six working standards made up in methyl-tert-butyl ether (MTBE) containing the target pesticides, internal standard and surrogate standard on the tuned GC-MS instrument (Figure 3-5 and Table 3-6) showing clear positive calibration curves with R^2 values of 0.971 and 1.

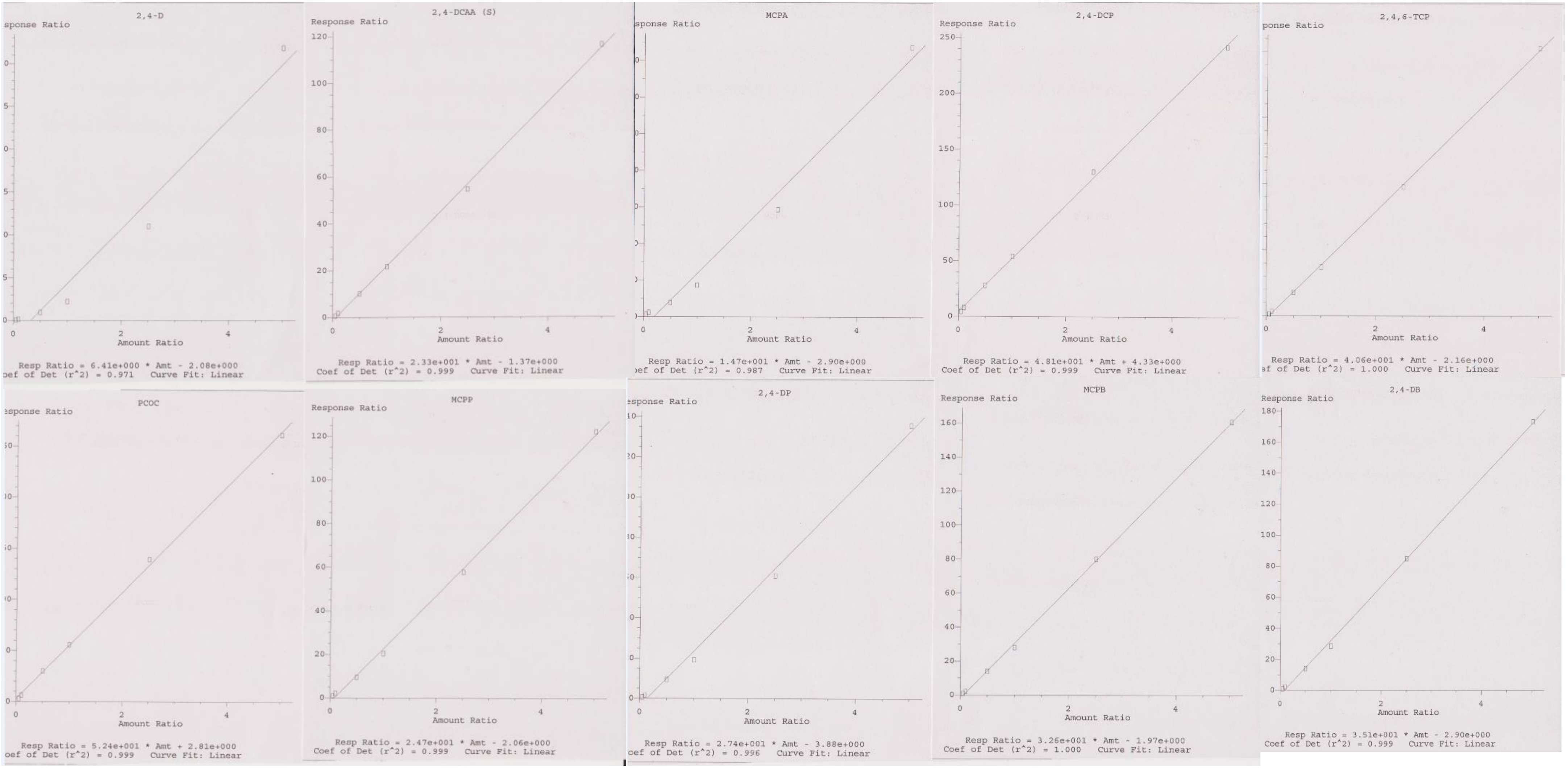

Figure 3-5. Calibration curves of phenoxy acids, dichloro acids and surrogate standard.

Table 3-6. Coefficient of determination (R2) of the pesticides and surrogate standards.

Compound	R^2
PCOC	0.999
2,4-DCP	0.999
2,4,6-TCP	1.000
MCPP	0.999
MCPA	0.987
2,4-DP	0.996
2,4-D	0.971
MCPB	1.000
2,4-DB	0.999
DCAA (S)	0.999

A calibration table was generated; each data file was quantified using the "Calculate and Generate" function in the MS ChemStation software. Individual peak integration was reviewed manually to ensure proper baseline integration. Quantification of a compound was based on the peak area of the primary ion (Quantification Ion) (Table 3-7). The primary ion was typically used, as it was the most abundant, to confirm the correct compound a confirmation ion was used.

Table 3-7. Quantitation ion and confirmation ion with internal standard used for quantification of the target pesticides.

Compound Name	Quantitation Ion (m/z)	Confirmation Ion (m/z)	Internal Standard for Quantitation
PCOC	156.1	141.0, 77.1	2,3,4,5-Tetrachlorophenol
2,4-DCP	176.0	161.0, 133.0	
2,4,6-TCP	195.0	197.0, 210.0	
MCPP	169.1	142.0, 228.1	
MCPA	214.1	141.0, 155.0	
2,4-DP	162.0	189.1, 248.0	
2,4-D	199.1	175.1, 234.1	
MCPB	101.2	59.1, 142.0	
2,4-DB	101.1	59.1	
DCAA (S)	173.0	197.1	

*(S) – Surrogate standard

3.5 Conclusion

A successful, efficient and reliable method with LOD in the range of 0.22-0.61 mg/L was developed for the HPLC when used for quantifying pesticide concentration in the range of mg/L.

When quantifying low pesticide concentrations GC-MS was required. The extraction method, using the Sep-Pak vac 6cc (500 mg) cartridges resulted in high recoveries and reproducible results. The method developed was successful and simpler when compared to some existing literature. LOD for the GC-MS were between 0.5 -1.0 mg/L for the targeted pesticides. Pesticides were still able to be quantified due to the 100 fold concentration via SPE.

3.6 References

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Evaluation of different treatment processes to remove chlorinated pesticides from an industrial production wastewater

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4.1 Abstract

Biological (aerobic and anaerobic), physical (granular activated carbon and biochar) and chemical processes (Fenton and UV/H_2O_2) were investigated for their ability to remove 2,4-dichlorphenoxy acetic acid (2,4-D); 4-(2,4-dichlorphenox) propionic acid (2,4-DP); 4-(2,4-dichlorophenox) butyric acid (2,4-DB); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy) butyric acid (MCPB) and 2-(4-chloro-2-methylphenoxy) propionic acid (MCPP) from a high strength pesticide production wastewater. Aerobic respirometry tests showed that wastewater was toxic to the activated sludge microorganisms at dilutions >25%. Optimisation of aerobic processes was achieved by adding nutrients (NH_4 and PO_4) and alkalinity. Cyclic tests showed reduced biomass acclimatisation after 103 days. The pesticides removal with the acclimatised biomass and nutrient and alkalinity dose reached 63% for phenoxy acids (MCPB, MCPA, PCOC, MCPP), 34% for 2,4,6-TCP and 17% for dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP). Anaerobic treatability tests indicated that the wastewater was toxic to organism present in anaerobic digested sludge, as no methane production was observed at dilutions >1%. Batch tests studies were completed to determine isotherms and understanding of the pesticide production wastewater by GAC adsorption. Lab-scale column tests showed regeneration was required between 599-1374 bed volumes (BV) when using 3, 5, 10 and 30 minutes empty bed contact time (EBCT). Advanced oxidation processes (AOPs) showed no removal of pesticides when using Fenton process at pH 2.8 and H_2O_2 at 1250 mg/L and 6250 mg/L with doses of Fe^{2+} at 5 mg/L, 20 mg/L and 50 mg/L. Low removal levels with UV/H_2O_2 also observed for doses of 1250 mg/L and 6250 mg/L with

a UV intensity of 3 mW/cm^2. On the other side, UV alone was effective breaking down the pesticides. Overall the results demonstrate that the pesticides could be removed to various degrees, using biological processes (after wastewater dilution to >25%) adsorption with GAC and photolysis with UV. Adsorption with biochar and advanced oxidation processes based on H_2O_2 were not suitable to treat the high strength pesticide production.

4.2 Introduction

Industrial wastewater can be challenging to treat due to its variability and the high concentrations of pollutants present. The pesticide production industry produces a complex wastewater with high strength containing toxic compounds such as 2,4, dichlorphenoxy acetic acid (2,4-D); 4-(2,4 dichlorphenox) propionic acid (2,4-DP); 4-(2,4, dichlorophenox) butyric acid (2,4-DB); 2,4 dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy) butyric acid (MCPB) and mecoprop (MCPP) in the range of mg/L. Characteristics of pesticide production wastewater have been scarcely reported, even though the pesticide production worldwide reached 2.3 million tons in 2007 (Grube et al, 2011). Chemical oxygen demand (COD) concentrations vary between sites and have been reported at 2500-5000 mg/L (Jin et al., 2010) up to 33700 mg/L (Chen et al., 2007). Pesticide concentrations have been reported up to 2020 mg/L (MCPA) in landfill leachate (Mcallister, et al, 1993).

There is very limited information on pesticide production wastewater treatment, but it typically takes place through biological treatment using activated sludge processes (ASP) combined with either physical processes such as adsorption, filtration or coagulation (Mcallister *et al.*, 1993; Bernhard, Muller and Knepper, 2006; Soares, 2015). Application of physical processes, more specifically, adsorption with activated carbon (AC) has increased over a number of decades for the removal of pollutants in both industrial and domestic wastewaters (Bonvin et al., 2016; Foo & Hameed, 2010; Knopp et al., 2016; Mailler et al., 2016; Ghoshdastidar et al., 2012).

The use of biological treatment allows pollutants to be degraded via microbial metabolic activity. When used to treat high strength wastewater containing toxic compounds, implementation of biological processes can be challenging due to the pollutants toxicity and resistance to microbial degradation (Jin et al., 2010; Lapertot et al., 2006). Mcallister et al. (1993) operated a laboratory scale continuous flow activated sludge unit to treat landfill leachate. The process consisted of a partitioned aeration tank with a hydraulic retention time (HRT) of 4.9h and solid retention time (SRT) of 35h. In the study more than 84% of the recalcitrant pesticides (2,4-D, MCPA, PCOC, 2,4-DCP and 2,4,5-TCP) were removed. Quan et al. (2004) acclimatised the activated sludge biomass to a synthetic mixture of pesticides in a conventional activated sludge system with and without bioaugmentation over a period of 6 months to determine the removal percentage of 2,4-DCP. Results showed the non-bioaugumented system removed 60.2% 2,4-DCP whereas bioaugmentation system removed up to 95.4% 2,4-DCP. Jin et al. (2010) carried out a study treating pesticide production wastewater using a pressurized activated sludge process with medium concentrations of COD (2500-5000 mg/L). In this study the traditional activated sludge process was modified to create a pressurised aerated tank to increase oxygen mass transfer. It was reported that when using a pressure at 0.30 MPa and an aeration time of 6h, the COD concentration was reduced from 500-5000 mg/L to 230-370 mg/L (85-92.5%).

Activated carbon can be applied in a number of forms, but the two most popular types are granular activated carbon (GAC) and powdered activated carbon (PAC). Granular activated carbon has higher initial costs due to the larger particle size enabling recovery and regeneration once full capacity has been reached. These larger pore sizes enable GAC to be more efficient than PAC at adsorbing heavy molecular weight pollutants (Aksu & Kabasakal, 2004; Areerachakul et al., 2007; Foo & Hameed, 2010). Activated carbon treatment process can be utilised as a pre or post treatment option; this is usually dependant on the composition of the wastewater being treated. Activated carbon has been effectively adopted to remove pesticides from water (Zümriye et al., 2005; Foo & Hameed., 2010; Hameed et al., 2009; Kim et al., 2008; Tuovinen et al., 1994). Tuovinen et al. (1994) studied the removal of the pesticides MCPP and 2,4-D in from industrial wastewater using GAC columns. The GAC was able to remove 88% MCPP in 7 days and 100% 2,4 in 4 days.

The use of chemical processes offers an alternative option to remove recalcitrant pesticides in wastewater via chemical oxidation. Over recent decades advanced oxidation processes (AOPs) have received significant attention for their high effectiveness removing recalcitrant pollutants in both industrial and domestic wastewaters (Badawy et al., 2006; Barbusiński & Filipek, 2001; Irmak et al., 2004; Irmak et al., 2006; Kowalska et al., 2004; Lafi & Al-Qodah, 2006; Mokrini et al., 1997). Advanced oxidation processes are able to achieve this by generating hydroxyl radicals which are non-selective and highly reactive (García-Montaño *et al.*, 2006; Lafi and Al-Qodah, 2006; Comninellis *et al.*, 2008). Removals between 51.4% to 100% (2,4-D and PCOC) had been achieved utilising various AOPs including UV/TiO_2 (Irmak et al., 2004), UV/H_2O_2 (Kowalska *et al.*, 2004) and Fenton process (Barbusiński and Filipek, 2001; Barbusiński, 2005). However AOPs have been mainly tested at lab and pilot scale due to costs and loss of efficiency at full scale. However, ozonation, UV/H_2O_2 has been successfully implemented at full scale as well as Fenton process, but there is little existing literature on this.

The majority of research to date focusses on the removal of one to four different pesticides (2,4-D, 2,4-DCP, MCPA and PCOC) on synthetic pesticide wastewater at laboratory scale studies, in hence with limited practical application (Fontmorin et al., 2013; Irmak et al., 2004; Kowalska et al., 2004; Mcallister et al., 1993; Quan et al., 2004). Existing reports has shown that individual or mixes of 2-4 pesticides can be treated using different types of biological (Mcallister *et al.*, 1993; Bernhard et al.,2006), physical (Aksu and Kabasakal, 2004) and chemical treatment processes (Vilar *et al.*, 2012; Cheng *et al.*, 2015). Nevertheless, the pesticide production wastewater investigated in this study is high strength, complex and variable containing various pesticides at a wide range of concentrations. Hence , the objective of this study was to evaluate and establish pesticide removal (2,4-D; 2,4-DP; 2,4-DB; 2,4-DCP; 2,4,6-TCP; PCOC; MCPA; MCPB and MCPP) using biological, adsorption and chemical processes.

4.3 Material and Methods

4.3.1 Materials

Chemicals; 2,4-D (99+%), 2,4-DCP (99%), 2,4-DP (98%), 2,4,6-TCP (98%) and PCOC (97%), iron sulphate, hydrogen peroxide (30%), ammonium chloride, sodium phosphate and sodium carbonate were purchased from Fisher Scientific (UK), 2,4-DB was purchased from VWR (UK) and MCPA (100%), MCPB (100%) and MCPP (100%) were purchased from Sigma-Aldrich (Germany). All solvents were high performance liquid chromatography (HPLC) grade. Granular activated carbon (GAC) (F-400) was purchased from Envirochem (UK) with a particle size between 0.5–1 mm. The media was sieved and washed with deionised water and ethanol. Biochar was obtained from a full scale advanced thermal combustion process in a domestic wastewater treatment plant (WWTP) processing sewage sludge (UK).

The pesticide production wastewater was sourced from a pesticide formulation factory producing a range of chlorophenoxy herbicides in the United Kingdom (UK). Activated sludge biomass for seeding the biological process, was sourced from a full scale WWTP with a 760,000 population equivalent treating domestic wastewater (UK). Anaerobic digested sludge was sourced from a anaerobic digester stabilising sludge from a full-scale domestic wastewater treatment plant (UK).

4.3.2 Biological Experiments

[redacted] Respirometry Tests

Respirometry is a standard technique that measures the oxygen uptake rate of an aerobic microbial population under controlled conditions and has been utilised in many studies to evaluate toxicity and biodegradability of various industrial wastewaters containing recalcitrant pollutants such as pesticides and pharmaceuticals (Meriç *et al.*, 2003; Kungolos, 2005; Farré *et al.*, 2007; Ballesteros Martín *et al.*, 2010). This technique is based on the fact that oxygen consumption is proportional to bacterial activity. Changes in oxygen uptake can occur in the presence of toxic compounds or other inhibitory conditions. When a toxic compound is present in wastewater the oxygen uptake is reduced and this can be easily measured in a respirometer. Once the respirometer tests have been completed, batch tests are useful to measure the removal of pesticides over time and establish effluent quality.

Respirometry tests were completed in a manometric respirometer (Environmental Services Ltd, Cornwall, UK) according to Raper et al, (2017) to determine the biodegradation and toxicity of the pollutants in the pesticide production wastewater towards the aerobic activated sludge microorganisms. The tests were completed by adding pesticide production wastewater to 500 mL GL45 Duron glass bottles (VWR, UK) and inoculated with activated sludge biomass. Mixing was provided by magnetic stirrer bars (35 x 7 mm PTFE coated bars) at a speed of 400 rpm and the temperature was kept at 22^{o}C using a water bath. Control tests comprised deionised water and the same amount of ASP sludge, from the same source. Deionised (DI) water was used has it has very limited nutrients, minerals and contaminants.

A number of experiments were completed in order to investigate toxicity, the impact of MLSS and the impact of nutrients and alkalinity addition. These tests were completed with different batches of pesticide production wastewater, collected at different times. Hence some variability between the tests and results was anticipated due to the variable wastewater quality.

The first experiment (*Test 1*) was used to evaluate toxicity to the AS and the experimental design is described in Table 4-1. In *Test 1* an MLSS of 600 mg/L was aimed at mimicking an ASP with low sludge retention time (SRT). All tests were carried out in duplicate.

Table 4-1. Experimental design for respirometry test to investigate toxicity: Test 1.

	mL		
Tests	**WW**	**DI water**	**Activated sludge biomass***
Control 1 (DI + Sludge)	0	405	45
100% WW + Sludge	405	0	45
75% WW + Sludge	304	101	45
50% WW + Sludge	202	202	45
25% WW + Sludge (a)	101	303	45

*final MLSS 600 mg/L in the bottle; WW- pesticide production wastewater

The second test (*Test 2*) was completed to evaluate the toxicity of the pesticide production wastewater to AS biomass at high MLSS (7000 mg/L) at different dilutions and also to assess the impact on addition of nutrients and alkalinity. Nutrients and alkalinity were also added to some bottles to achieve the ratio C:N:P of 100:5:1. The chemicals added were: ammonium chloride: 0.9 g/L, monosodium phosphate dihydrate: 0.18 g/L and sodium carbonate: 0.3 g/L (Table 4-2). In *Test 2* an MLSS of 7000 mg/L was aimed at mimicking an ASP with high SRT or a membrane bioreactor (MBR). All tests were carried out in duplicate.

Table 4-2. Experimental design for respirometry test to investigate toxicity and impact of nutrients and alkalinity addition: Test 2.

	mL		
Tests	**WW**	**DI water**	**Activated sludge biomass***
Control 2 (DI + Sludge)	0.0	65.0	15
100% WW + Sludge	65.0	0.0	15
25% WW + Sludge (b)	16.2	48.7	15
10% WW + Sludge	6.5	58.5	15
1% WW + Sludge	0.6	64.3	15
10% WW + Sludge + Nutrients + Alkalinity	6.5	58.5	15

*final MLSS 7000 mg/L in the bottle; WW- pesticide production wastewater

[redacted] Biological treatability: Pesticide removal tests

Biological treatability tests were completed to determine the removal of pesticides in the pesticide production wastewater. Activated sludge biomass was mixed with wastewater at various dilutions (25-40%) and nutrients; ammonium chloride (1.7-4.4 g/L) and monosodium phosphate (dihydrate) (0.2-0.6 g/L) and alkalinity; sodium carbonate (0.1-0.5 g/L) were added and shaken for 7 days using an orbital shaker (SHAKA5000, Thermo Scientific) and incubated at room temperature (18-20°C). Daily samples were taken and filtered before analysed on the HPLC.

[redacted] Biological treatability: Acclimatisation to pesticide production wastewater

The aim of this study was to investigate if the ASP sludge could be acclimatised to the wastewater pollutants and higher removals of pesticides could be obtained by continued contact. Batch tests were completed in conical flasks with pesticide production wastewater at 25%, with addition of nutrients and alkalinity (ammonium chloride 3.40 g/L + monosodium phosphate dihydrate) 0.46 g/L and sodium carbonate (0.1 g/L) and AS biomass at an MLSS of 7000 mg/L. The conical flasks were incubated for 3-7 days in an orbital shaker (SHAKA5000, Thermo Scientific) at room temperature. After 4-7 days (1 cycle) the sludge was allowed to settle, the wastewater was decanted and fresh wastewater was added. Samples were taken at the end of each cycle for pesticide analysis in the HPLC. These tests were completed with different pesticide production wastewater batches of water, collected at different times. Hence some variability between the tests and results was anticipated due to variable wastewater quality.

[redacted] Anaerobic treatability

The biological methane production tests were completed by mixing anaerobic digested sludge (20% of total volume) with pesticide production wastewater at different dilutions, in 120 mL serum bottles with rubber stoppers and shaken for 15 days using an orbital shaker (SHAKA5000, Thermo Scientific) and incubated at room temperature. Additional nutrients (ammonium chloride 3.4 g/L and monosodium phosphate dihydrate 0.9 g/L) were added to give the ideal C:N:P ratio of 100:5:1 and 300 mg/L alkalinity (sodium carbonate). The pressure in the headspace was checked daily using a gas pressure gauge and 1 mL samples of the gas phase were analysed via GC–CSI 200 (Cambridge Scientific Instruments Ltd, UK) for the methane composition. Control tests were also included and these comprised of the same anaerobic sludge and deionised water.

4.3.3 Physical processes

[redacted] Equilibrium tests for GAC and biochar

Stock solutions of all target pesticides were prepared in methanol except PCOC prepared in water and stored at 4°C. Stock solutions were removed from fridge and left for an hour to reach room temperature, reweighed to check for evaporation and sonicated for 2-3 minutes to make sure all pesticides were dissolved. Synthetic batch experiments were carried out using the stock solutions and used to make up six identical synthetic solutions containing the average concentrations (5-550 mg/L) of the pesticide production wastewater in conical flasks. Once all chemicals were added, each conical flask was made up to 250 mL with deionised water and left over night to allow the methanol to be evaporated before being topped back up to 250 ml. Depending on the experiment, known amounts of F-400 GAC (0.25-50 g/L) or biochar (1-50 g/L) (with particle sizes 500 µm and 53-63 µm) were added to the samples. The biochar had an average particle size of 500 µm and it was grinded and sieved to achieve smaller particles sizes of 53-63 µm. Five millilitre samples were taken and filtered (0.45 µm) into 1 mL HPLC vials at 30 minutes, 1, 5, 8 and 24 hours of incubation. Samples were analysed on the HPLC. Batch tests were also completed with the pesticide production wastewater. The tests were carried out by adding a known amounts of GAC or biochar (average particle size 500 µm), to the pesticide production wastewater (250 mL). Five millilitre samples were taken and filtered into 1 mL HPLC vials at 30 minutes, 1, 5, 8 and 24 hours of incubation. Samples were analysed on the HPLC.

[redacted] Column experiments using GAC

Continuous flow column experiments were completed in glass columns of 41 cm length and 3 cm internal diameter, filled with 7.5 g F-400 GAC with a particle size between 0.5–1 mm. The media was sieved and washed with deionised water and ethanol. The pesticide production wastewater flow was adjusted in order to achieve the specified empty bed contract times (EBCT) of 3, 5, 10 and 30 minutes. The experiments were carried out at room temperature (18-20°C). Samples were collected at regular intervals throughout the experiment and filtered before been analysed on the HPLC. The column experiment was stopped when breakthrough was achieved. Breakthrough was achieved when the pesticides concentration was the same in the effluent as in the influent.

The capacity of the GAC and length of unused bed was obtained from the breakthrough curves for the corresponding pesticide that reached breakthrough first for each EBCT. The time in which breakthrough was reached (t_u) and the time for the GAC to be saturated (t_t) was calculated using equations 4-1 and 4-2.

$$t_u = \int_o^{t_b} \left(1 - \frac{C}{C_o}\right) dt \quad \textbf{(Equation 4-1)}$$

$$t_t = \int_o^{\infty} \left(1 - \frac{C}{C_o}\right) dt \quad \textbf{(Equation 4-2)}$$

Where t_b is the time when breakthrough occurs, C is the concentration measures at time (t) and C_o is the initial concentration of the influent.

From this, the length of unused GAC bed can be calculated from equation 4-3.

$$\boldsymbol{H_{UNB}} = \left(\mathbf{1} - \frac{\boldsymbol{t_u}}{\boldsymbol{t_t}}\right)\boldsymbol{H_t} \quad \textbf{(Equation 4-3)}$$

Where H_{UNB} is the length of the unused GAC bed and H_t is the total GAC bed length.

The time required for breakthrough and saturation to be reached is related to GAC capacity used and GAC saturation capacity (equation 4-4 and 4-5).

$$q^* = \frac{C_o Q}{1000\, m_s} \int_0^{t_t} \left(1 - \frac{C}{C_o}\right) dt \quad \textbf{(Equation 4-4)}$$

$$q = \frac{C_o Q}{1000\, m_s} \int_0^{t_u} \left(1 - \frac{C}{C_o}\right) dt \quad \textbf{(Equation 4-5)}$$

Where q and q* are capacity used and saturation capacity, C_o is the initial concentration of the influent, Q is the flow and m_s is the mass of the GAC.

4.3.4 Chemical processes

[redacted] Fenton process experiments

Pesticide production wastewater and synthetic pesticide solutions were adjusted to pH 2.8 using 1 M sulphuric acid. Iron sulphate (between 5-50 mg/L) and hydrogen peroxide (between 100-12500 mg/L) was also added (Table 4-3). Mixing was provided by a stirrer plate and the experiments were carried out in a dark room to prevent UV light aiding the process. Samples were taken over a period of 1 hour and filtered through a 0.45 µm syringe filter (Millex-HA). The reaction was stopped by using acetonitrile as a quenching agent since it acts as a radical scavenger, before being analysed on the HPLC.

Table 4-3. Fenton experiments carried out on synthetic pesticide solution and pesticide production wastewater.

	H_2O_2 Dose (mg/L)				
		100	**1250***	**6250**	**12500**
Fe^{2+} Dose (mg/L)	**5**	WW	WW	-	-
	20	-	WW Syn	Syn	WW
	50	-	-	Syn	-

WW – Real pesticide production wastewater, Syn – Synthetic pesticide solution

* - theoretical oxygen demand of H_2O_2 required to remove the targeted pesticides

[redacted] UV/H_2O_2 experiments

Hydrogen peroxide at 1250 mg/L (i.e., the theoretical oxygen demand w of H_2O_2 required to removal the targeted pesticides) and 6250 mg/L were spiked into synthetic pesticide solution or pesticide production wastewater in a 100 ml petri dish with a UV light intensity at 3 mW/cm^2. All experiments were conducted in a Wedeco AG bench scale quasi-collimated beam apparatus (Herford, Germany) equipped with four 30 W UVC low pressure lamps which emits a monochromatic light a wavelength of 254 nm. Samples were mixed using a stirrer plate at room temperature, 20°C and carried out in a dark room. Samples were taken over a period of 1 hour and filtered through a 0.45 µm syringe filter (Millex-HA). The reaction was stopped by using acetonitrile as a quenching agent since it acts as a radical scavenger, before been analysed on the HPLC.

4.3.5 Analysis

[redacted] Wastewater characterisation - biological tests

COD, BOD, NH_4, PO_4 of the pesticide production wastewater were analysed using cell tests according to the Millipore manufacture instructions.

HPLC

The HPLC analyses were carried out in a Shimadzu DGU-20A5 (Shimadzu, Japan) HPLC equipped with a UV detector (series SPD-20A). A Fortis Cyano 250 mm x 4.6 mm, 5µm column (Chromex Scientific, UK) with a corresponding 2 cm cartridge guard column (Chromex Scientific, UK) was used. The detector was set at 280 nm and the flow rate and injection volume were 1 ml/min and 50 µl, respectively. The column temperature was set to 20°C. The mobile phase consisted of 70% deionised water and 30% acetonitrile + 0.4% acetic acid. The analysis ran for 25 minutes.

4.4 Results and Discussion

4.4.1 Pesticide production wastewater characterisation

The quality of the pesticide production wastewater varied significantly over the sampling period (Table 4-4). The BOD and COD concentrations ranged from 5101-18000 mg/L and 18675-47763 mg/L, respectively. Others also report that the pesticide production wastewater contained high COD with concentrations up to 33700 mg/L (Cheng et al., 2015). The average COD/BOD ratio indicated that the wastewater had poor biodegradability with a ratio of 3.08. A ratio of 3 or lower often indicates that the wastewater is biodegradable and can be treated with biological processes; however, this ratio does not directly imply that the biological treatment will be successful (Vollertsen and Hvitved-Jacobsen, 2002). On the other side, ammonia and phosphate concentration were low, resulting in a carbon:nitrogen:phosphate ratio of 22930:15:1, indicating that additional nutrients and alkalinity are likely to be required to increase the efficiency of the biological treatment. (Table 4-4). A C:N:P ratio of 100:5:1 is recommended for sustaining biological activity (Water Environment Federation, 2008).

The pesticides concentrations in the wastewater were highly variable across the 12 sampling campaigns carried out. These results were expected, as the pesticide production facility manufactures different formulations at different intervals of time, depending on customer demand, generating variability in the wastewater quality produced. Average concentrations of 2,4-DCP were high at 58.96 mg/L, followed by MCPA at 32.45 mg/L, PCOC with 21.91 mg/L, 2,4-D at 13,94 mg/L and MCPP at 7.58 mg/L. On the other side the average concentrations for 2,4-DB and 2,4,6-TCP were <5 mg/L and the average concentrations for 2,4-DP and MCPB were <1 mg/L. Characteristics of pesticide production wastewater have been scarcely reported, so it is not possible to comment on how these values compare with other studies.

Other important parameters measured in wastewater that have a major relevance when investigating treatment processes are the total suspended solids (TSS) and volatile suspended solids (VSS). Based on the high concentrations of TSS measured at 1437 mg TSS/L, it is recommended to implement a solids separation process (such as settling tank, lamella settler or micro-screen). The ratio between TSS and VSS indicates that the solids are mostly inorganic, also emphasizing the need for a solids separation stage.

Table 4-4. Pesticide production wastewater characterisation.

	Sample (n=12)		
	Average and standard deviation	Max	Min
BOD (mg/ L)	11590 ± 3488	18000	5101
COD (mg/ L)	33750 ± 12996	47763	18675
COD/BOD*	3.08 ± 1.19	5.33	1.95
pH	6.5 ± 0.1	6.8	6.3
Alkalinity (mg CaCO3/L)	1069 ± 624	1671	151
Total suspended solids (mg/ L)	1437 ± 651	2284	688
Volatile suspended solids (mg/ L)	204 ± 97	375	107
Ammonium (mg/ L)	19.1 ± 20.9	67.4	0.6
Phosphate (mg/ L)	2.5 ± 1.7	6.45	0.7
C:N:P Ratio	22930:15:1		
Pesticides			
2,4-D (mg/ L)	13.94 ± 18.46	42.16	<0.18
2,4-DB (mg/L)	1.36 ± 1.09	3.61	0.2
2,4-DP (mg/ L)	0.12 ± 0.28	0.9	<0.23
2,4-DCP (mg/L)	58.96 ± 36.04	106.5	0.1
2,4,6-TCP (mg/L)	3.26 ± 2.19	4.11	0.3
MCPA (mg/L)	32.45 ± 19.65	50.69	0.1
MCPB (mg/L)	0.30 ± 0.35	1.1	<0.28
MCPP (mg/L)	7.58 ± 6.06	18.17	0.2
PCOC (mg/L)	21.91 ± 11.32	39.65	0.14

*COD/BOD of 3 indicates poor biodegradability; n – number of samples.

4.4.2 Biological process tests

Aerobic – Respirometry Tests

Figure 4-1a shows the oxygen uptake of the different concentrations of wastewater (100%, 75%, 50%, 25% and 0% - Control) for the period of 7 days at an MLSS concentration of 600 mg/L. During this period, the control sample containing 100% deionised water and AS consumed 115 mg/L O_2. For the different dilutions of wastewater 100%, 75%, 50%, 25%, the oxygen consumption was 35, 23, 23 and 27 mg/L O_2, respectively. From this, the oxygen uptake rate (OUR) was calculated: for wastewater dilutions of 25%, 50%, 75% and 100% the OUR results were 0.123, 0.102, 0.107 and 0.161 mg O_2/h.L, respectively (Table 4-5). These OUR values were below the control test of 0.454 mg O_2/h.L, indicating microbial inactivation and toxicity.

Test 2 (Figure 4-1b) shows the oxygen uptake of the different concentrations of wastewater used (control, 1%, 10%, 25%, 10% with additional nutrients and alkalinity) for the period of 5 days at an MLSS of 7000 mg/L. During this period a total of 71 mg/L O_2 were consumed in the control bottles. For the different dilutions of pesticide production wastewater of 1%, 10%, 25%, 10% with additional nutrients and alkalinity, oxygen consumed was 74, 152, 252, and 203 mg/L O_2, respectively. In *Test* 2, with high MLSS, the OUR at 1%, 10% and 25% were 0.517, 0.985 and 1.022 mg O_2/h.L, respectively. These were higher than the control of 0.464 mg O_2/h.L (Table 4-5), indicating no toxic effect on the microorganisms. Hence it can be established that the pesticide production wastewater was not toxic at concentrations >25%, if high MLSS concentrations are ensured. However, it is necessary to consider the fact that different dilutions of the pesticide production wastewater would lead to different initial COD concentrations and therefore without inhibition would give different OURs. For instance, in Figure 4-1b and Figure 5-4, these results suggest that the microorganisms are partially inhibited by more concentrated pesticide production wastewater as higher COD concentrations should lead to higher OURs. Therefore normalisation of the data to the initial COD should be considered. Pai et al., (2009) studied the growth of activated sludge in organophosphate pesticides using the respirometer, when adding 0.5 mg/L of pesticides glyphosate or malathion or combined. The results showed a decrease of biological activity by 62%, 66% and 49%, respectively.

With higher MLSS concentrations (7000 mg/L) the aerobic sludge microorganisms are more resistant to shock loads (Stephenson et al., 2000).

This can be obtained in long SRT ASP or then in membrane bioreactor (MBR) processes (Bernhard et al., 2006). When comparing the OUR of the tests, the 10% wastewater dilution with additional nutrients and alkalinity, the OUR was higher with 1.274 and 0.985 mg O_2/h.L respectively. By adding the additional nutrients (nitrogen and phosphate) the recommended C:N:P of 100:5:1 was achieved (Water Environmental Federation, 2008). Ammonia and phosphate are essential nutrients for all living organisms and are used in microbial cells to maintain biochemical activity (Tchobanoglous et al., 2003). Alkalinity was added to maintain a stable pH as the most effective pH for most microorganisms is around pH 7. In order to maintain optimal pH sufficient alkalinity present (Marietta, 2014).

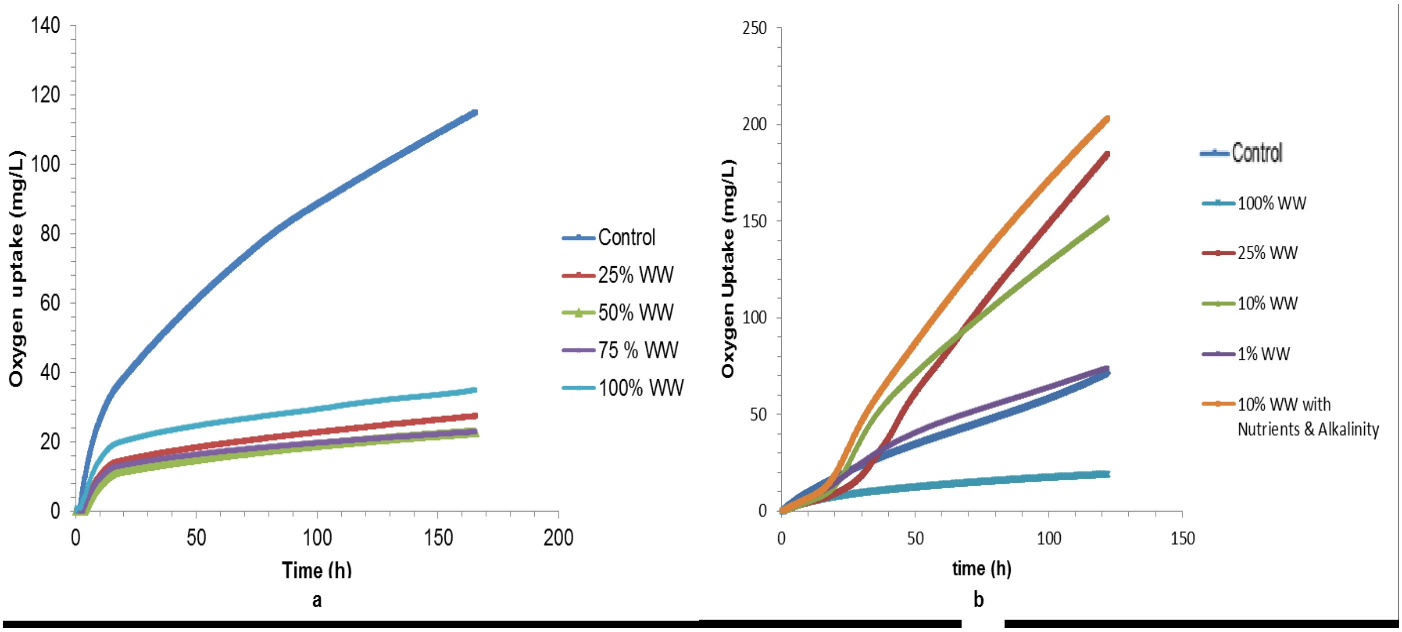

Figure 4-1. Oxygen uptake measured by the respirometer for Test 1 (a) and Test 2 (b) at different dilutions of the pesticide production wastewater. All tests were carried out in duplicate. Test 1 AS MLSS – 600 mg/L. Test 2 AS MLSS – 7000 mg/L.

Table 4-5. Oxygen uptake rate (OUR) calculated from the respirometer data for Test 1 and Test 2 for different dilutions of the pesticide production wastewater. All tests were carried out in duplicate.

	Wastewater dilution (%)	Respirometry OUR (mg O_2/h.L)
Test 1 **(AS MLSS = 600 mg/L)**	100	0.161 ± 0.07
	75	0.107 ± 0.001
	50	0.102
	25	0.123 ± 0.004
	Control 1*	0.454
Test 2 **(AS MLSS = 7000 mg/L)**	100	0.151
	25	1.022 ± 0.391
	10	0.985 ± 0.014
	1	0.517 ± 0.028
	10 N + A (addition nutrients and alkalinity)**	1.274
	Control 2*	0.464

*Control contained deionised water and activated sludge.

**Additional nutrients were added to the wastewater to achieve a C:N:P ratio of 100:5:1, so the following was added: : ammonium chloride: 0.9 g/L, monosodium phosphate dehydrate: 0.18 g/L and sodium carbonate: 0.3 g/L.

[redacted] Biological treatability: Pesticide removal tests

To determine the fate of pesticides, batch tests were completed with pesticide wastewater dilutions 25%, 30%, 35% and 40% inoculated with activated sludge biomass (Figure 4-2). Removal of phenoxy acids (MCPB, MCPA, PCOC, MCPP) were 37% (25% WW), 39% (30% WW), 9% (35% WW) and 18% (40% WW). Removal of dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP) were -64% (25% WW), -82% (30% WW), -399% (35% WW) and -383% (40% WW). The negative removals of dichloro acids were due the accumulation of 2,4-DB. This could be due to other larger compounds (e.g.: 2,4-D-isopropylester, not targeted in this study) breaking down into 2,4-DB. Removal of 2,4,6-TCP was 30% (25% WW), -16% (30% WW), -58% (35% WW) and -19% (40% WW). Overall the results show that the higher pesticide removals were achieved for 25% wastewater dilution.

Figure 4-3 shows the pesticide removal after adding different concentrations of nutrients and alkalinity to the pesticide production wastewater at 25% dilution. The addition of a combination of nutrients and alkalinity to the wastewater resulted in the greatest pesticide removal efficiencies, suggesting it was the most effective treatment option (Figure 4-3). This could be due to the nutrients added in order to make the wastewater more suitable for microbial growth (Richard, 2003; Water Environment Federation, 2008). Adding low concentrations of alkalinity overall favoured pesticide removal, specially dichloro acids (2,4-D, 2,4-DP & 2,4-DB) and 2,4,6-TCP. Although dichloro acids concentrations increased in all experiments after biological treatment, this was due to a bioaccumulation of 2,4-DB, the lowest accumulation was observed when medium nutrients (to reach the ideal ratio C:N:P of 100:5:1) and alkalinity were added, hinting that the 2,4-D accumulation is related with some limitation in the microbial metabolism. As previously discussed, accumulation of 2,4-DB is thought to be related with the breakdown of a larger compound (such as 2,4-D-Isopropylester). Regarding the removals of phenoxy acids (MCPA, PCOC, MCPP & MCPB), no significant differences were noticed by adding additional nutrients at low, medium and high concentration.

Figures 4-2 and 4-3 show variation of pesticides concentrations due to the natural variability of the wastewater as tests were completed with different wastewater batches of water, collected at different times.

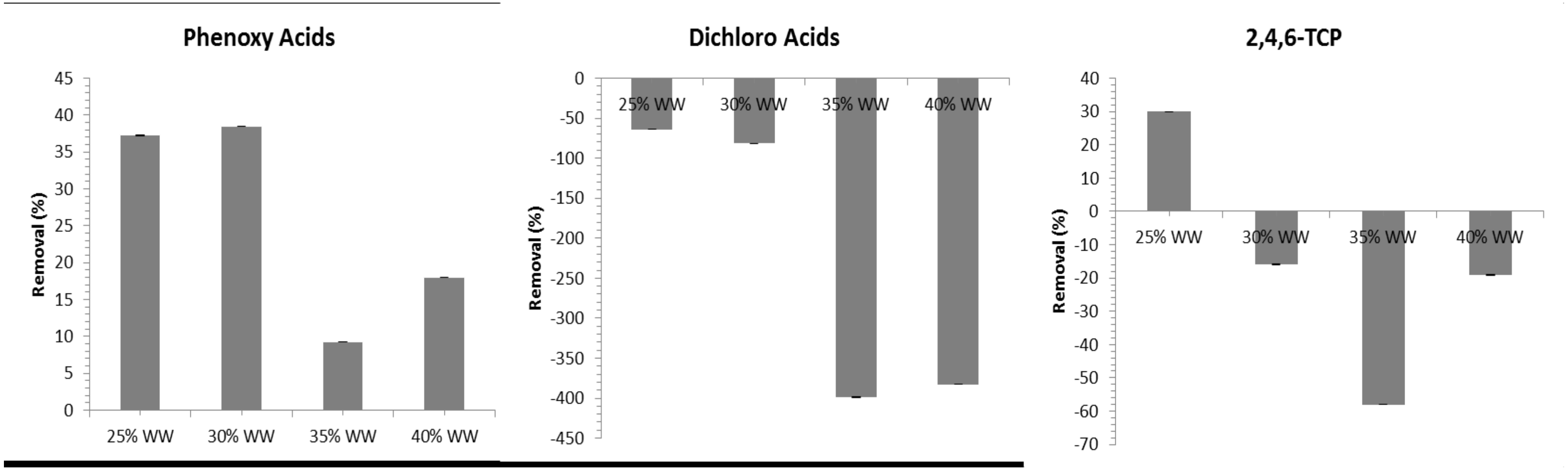

Figure 4-2. Pesticides removal in batch tests with AS at 7000 mg/L MLSS for phenoxy acids (MCPB, MCPA, PCOC, MCPP), dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP) and 2,4,6-TCP at different wastewater dilutions.

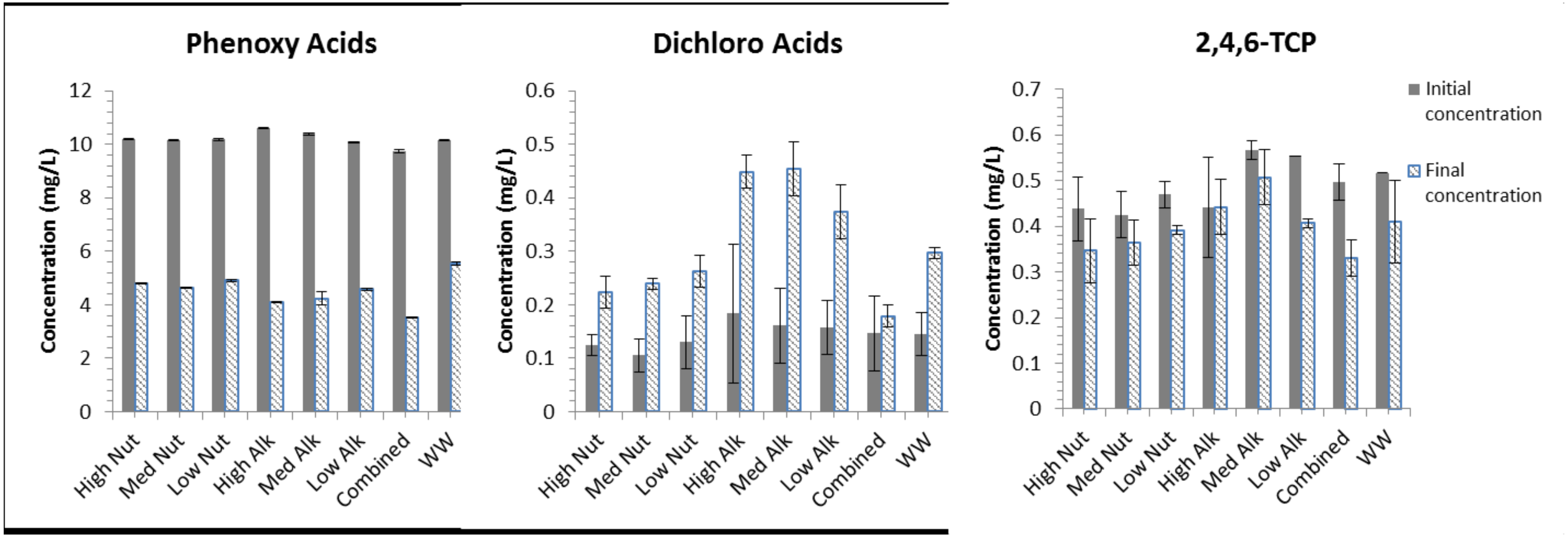

Figure 4-3. Pesticide concentrations in batch tests with AS at 7000 mg/L MLSS for phenoxy acids (MCPB, MCPA, PCOC, MCPP), dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP) and 2,4,6-TCP after adding different concentrations of nutrients and alkalinity to the pesticide wastewater at 25% dilution. High nutrients – ammonium chloride (4.42 g/L) + monosodium phosphate dehydrate (0.60 g/L); Medium nutrients (ideal ratio C:N:P (100:5:1) – ammonium chloride (3.40 g/L) + monosodium phosphate dihydrate (0.46 g/100 mL); low nutrients – ammonium chloride (1.70 g/L) + monosodium phosphate dihydrate (0.23 g/L); High alkalinity – sodium carbonate (0.5 g/L) Medium alkalinity – sodium carbonate (0.3 g/L) - Low alkalinity – sodium carbonate (0.1 g/L); Combined – Medium nutrients and Medium alkalinity.

[redacted] Biological treatability: Acclimatisation to pesticide production wastewater

To investigate the capacity of the activated sludge biomass to adapt to the pesticide production wastewater, and the potential to remove higher concentrations of pollutants, acclimatisation tests were completed. Acclimatisation is the process where the microorganisms adjust to a change in environment such as using the recalcitrant pesticides as a food source. The tests were completed with different wastewater batches, collected at different times and consequently the pesticides concentrations varied across the acclimatisation tests, making the results hard to interpret (Figure 4-4). After 14 cycles (a period of 103 days) the activated sludge biomass was able to progressively reduce the final concentrations of phenoxy acids and 2,4,6-TCP (Figure 4-4). The ability of microorganisms to produce higher effluent quality (e.g.: low concentration of pesticides) is related with microbial kinetics and the half saturation constant (Ks). Other researchers have indicated that a decrease in Ks values can be interpreted as biomass acclimatisation (King et al., 2012) although in this study this is not clear due to the wastewater variability. Average removal of phenoxy acids (MCPB, MCPA, PCOC, MCPP) was 63%, average removal of 2,4,6-TCP was 34% and average removal of dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4-DCP) was 17%. Most surprisingly, there was no accumulation of 2,4-DB, as shown in previous experiments (Figure 4-4). This could be due to the wastewater variability, or the AS biomass acclimatising to the wastewater pollutants. Although the results do not allow pointing out a single reason, it is believed that the dose of nutrients and alkalinity had a role to play. Quan, et al., 2004 estimated an acclimatisation period of 6 months for activated sludge towards the pesticide 2,4-DCP, but in this study, a period 3.4 months (103days) was not enough to observe clear biomass acclimatisation.

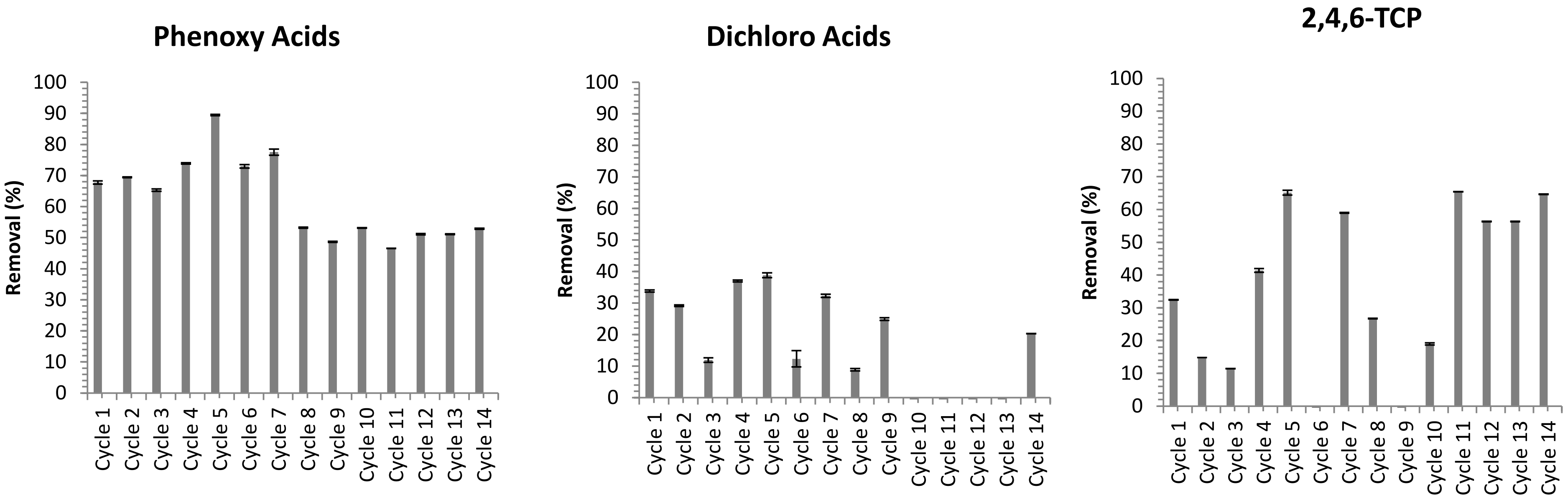

Figure 4-4. Pesticides removal in batch tests with same AS at 7000 mg/L MLSS over 14 cycles of 3-5 days for phenoxy acids (MCPB, MCPA, PCOC, MCPP), dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP) and 2,4,6-TCP Tests were completed with 25% pesticide production wastewater dosed with nutrients; ammonium chloride (1.70 g/L) + monosodium phosphate dihydrate (0.23 g/L) and alkalinity sodium carbonate (0.1 g/L).

[redacted] Anaerobic Experiments

Anaerobic treatment processes are commonly applied to treat high strength industrial wastewater. The methane production with the pesticide production wastewater at dilutions >10%, was less than 3% in the headspace of the serum bottles, whilst 9.2% was measured in the controls (Table 4-6). Hence it can be ascertained that the pesticide production wastewater was toxic to the anaerobic organisms at dilutions >10%. On the other side, at 1% wastewater the methane content increased to 15.9%, indicating no toxicity. However, it is necessary to consider the fact that different dilutions of the pesticide production wastewater would lead to different initial COD concentrations and therefore without inhibition would give different methane production. For instance, the more concentrated the pesticide wastewater the higher the initial COD concentrations which should lead to more COD been converted into methane. Normalisation of the data to the initial COD should have been considered. Although these results show potential for anaerobic treatment, 1% wastewater dilution would require very large reactors (high CAPEX) to treat wastewater with COD <300 mg/L, hence this process was not considered attractive for treating this wastewater.

Table 4-6. Methane composition in the headspace of the biological methane production tests with different dilutions of the pesticide production wastewater.

Wastewater concentration (%)	Methane composition in the gas phase (%)
100	0.5
75	0.6
50	0.6
25	0.7
10	3.0
1	15.9
10 (N + A) *	1.7
0 (Control)	9.2

*Additional nutrients and alkalinity were added to give the ideal C:N:P ratio of 100:5:1 and 300 mg/L (sodium carbonate)

4.4.3 Physical process tests

[redacted] Equilibrium tests for GAC and biochar

The aim of the experiments was to determine adsorption capacity, affinity (adsorption force of the adsorbate for the adsorbent) and selectivity of the GAC and biochar for the pesticides in production wastewater. Figure 4-5 (top) shows the capacity (q - the mass of pollutant adsorbed per mass of GAC) and the pesticide removal for tests completed with 0.5 g/L F-400 GAC and synthetic solutions. Figure 4-5 showed that most pesticides reached equilibrium within 5 hours and for PCOC, MCPB and 2,4-DP, equilibrium was reached at 1 hour. Within 24 hours, 4.8, 11.7, 45.4, 17.3, 25.6, 78.4, 287.7 and 24.1 mg/g of pesticides 2,4,-DP, MCPP, 2,4-DB, MCPB, MCPA, PCOC, 2,4-DCP and 2,4,6 –TCP, respectively were adsorbed, which corresponded to removals of 77%, 30%, 42%, 57%, 56%, 79%. 95% and 97%, respectively. Tests with F-400 GAC at doses greater than 1 g/L showed complete removal of, 2,4-DP; 2,4-DB; 2,4,6-TCP; PCOC MCPA; MCPB and MCPP within 24 hours.

Figure 4-5 (middle) shows the capacity (q) and the pesticide removals for tests completed with 1 g/L biochar and synthetic solutions. Equilibrium was reached within 5 hours and after 24hrs, on average 11% of the pesticides were removed. The highest removal percentage was obtained for 2,4,6-TCP at 19%. Kinetic experiments showed that within 24 hours and at 5 g/L, 10 g/L, 30 g/L and 50 g/L biochar doses, the average pesticide removals were 27%, 55%, 97% and 99%, respectively.

Existing literature shows that pesticides can be absorbed to GAC, although most of the studies are focused on synthetic solutions or weak wastewater. Aksu & Kabaskal (2005) carried out studies comparing laboratory scale activated carbon treatment with 2,4-D in synthetic wastewater. The study used 0.1 g AC in 100 ml solutions with 2,4-D at concentrations of 103.9, 190.4, 404 and 624.5 mg/L, shaken for a period of 2 days at a temperature of 25^{o}C The results showed q values of 98, 173, 340 and 470 mg/g, respectively. These q values were much higher than the values obtained in this study. This could be due to a single compound (2,4-D) being investigated, whereas this study was focused on a complex mixture of pesticides. Kim et al., (2008) studied F-400 GAC maximum capacities for 2,4-D and MCPP in synthetic solution, the maximum capacity observed was 411.13 mg/g and 389.20 mg/g, these also are significantly higher capacities than the ones obtained in this study with 2-4-D (>10.2 mg/g) and MCPP (>11.2 mg/g) however 2,4-DCP and PCOC reached capacities of 472 mg/g and 132.2 mg/g, respectively (Table 4-8).

Figure 4-5 (bottom) shows the capacity (q) and the pesticide removals for tests completed with 1 g/L F-400 GAC using pesticide production wastewater. Equilibrium was reached within 5 hours. After 24 hours the 1 g/L GAC removed 100% 2,4-D, 2,4,-DP, 2,4,6-TCP and 2,4-DB whereas MCPA, PCOC, 2,4-DCP and MCPP were removed by 82%, 97%, 98% and 81%, respectively. Higher removals were obtained after 48 hours, MCPA, PCOC, 2,4-DCP and MCPP were removed by 93%, 98%, 99% and 93%, respectively. At GAC doses of 0.05, 0.06, 0.19, 0.25, 0.5 and 0.75 g/L the pesticides were removed between 11-34% (0.05 g/L), 15-36% (0.06 g/L), 31-68% (0.19 g/L), 33-89% (0.25 g/L), 37-100% (0.5 g/L), 84-100% (0.75 g/L) and 99-100% (5 g/L) after 48 hours.

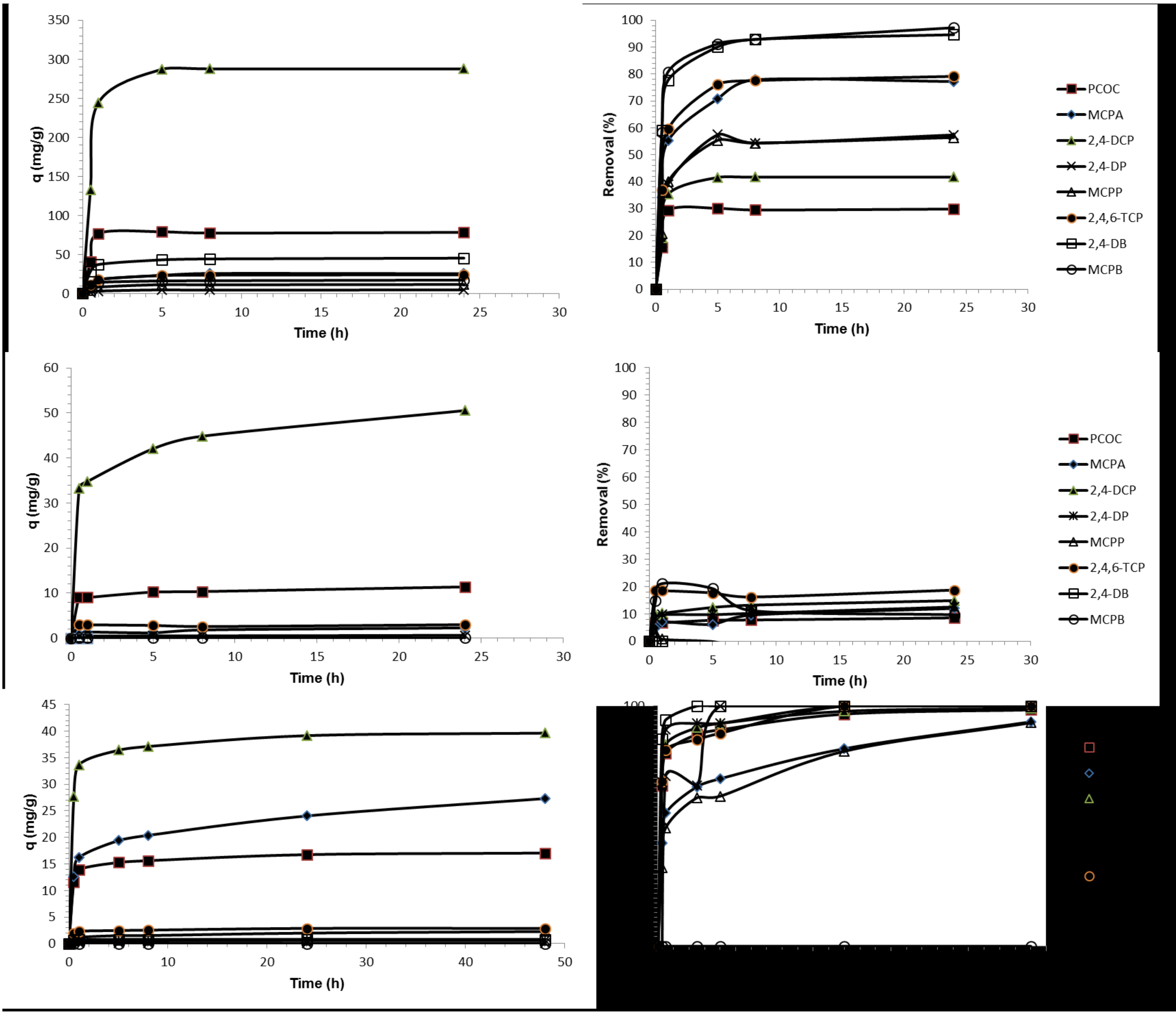

Figure 4-5. Adsorption capacity (q) and pesticide removals for tests completed with 0.5 g/L F-400 GAC (top) and 1 g/L of Biochar (middle) using synthetic pesticide solutions and 1 g/L F-400 GAC using pesticide production wastewater.

Table 4-7 shows the capacity (q) of 1 g/L F-400 GAC using synthetic pesticide solution and real pesticide production wastewater. In synthetic solution, the removals for MCPB, 2,4,-DP, 2,4,6-TCP and 2,4-DB were 100% and. The real wastewater contained no MCPB in this specific batch of wastewater. The results showed that GAC had the capacity to adsorb more pesticides (8 fold increase) in synthetic pesticide solution in comparison with the real wastewater. This was due the real wastewater containing other contaminants such as organic matter. This organic matter interferes with pesticide adsorption by been absorbed itself and reducing the GAC capacity, and therefore reducing the amount of pesticides that can be adsorbed. This had been seen in other existing literature where wastewater containing a variety of compounds have been treated with a hybrid system using GAC and MBR (Alrhmoun et al., 2014).

Table 4-7. GAC F-400 capacities for synthetic pesticide solution and real wastewater completed in 24 hours batch tests.

		GAC F400 dose 1 g/L	
	Compounds	**Synthetic**	**Real WW**
q (mg/g)	**2,4-D**		0.58
	MCPA	39.10	24.05
	PCOC	132.26	16.76
	2,4-DCP	472.27	39.16
	2,4-DP	>10.21	0.09
	MCPP	>17.75	2.00
	2,4,6-TCP	23.59	2.88
	2,4-DB	>16.33	0.81
	MCPB	>11.28	
	Total pesticides	667	86

Many studies have successfully applied the Freundlich adsorption models (Jusoh et al., 2011; Nalcaci et al., 2011; Sotelo et al., 2002) or Langmuir adsorption models (Hameed et al., 2009; Salman and Hameed, 2010; Jusoh *et al.*, 2011) on chlorinated pesticides.

The results displayed in Figures 4-5 and 4-7 were used to apply Freundlich and Langmuir models (Table 4-8). Any compounds reaching 100% removal before the equilibrium time were not used. During this experiment, the pesticide 2,4-D, 2,4-DP and MCPB were not present in the wastewater. The isotherms were assumed to fit the models by calculating the correlation coefficient (R^2) for each pesticide. It was assumed that an R^2 of > 0.85 would indicate a significant correlation. MCPA (R^2 = 0.964) was the only compound to fit the Langmuir model whereas MCPA (R^2 = 0.937) and 2,4-DCP (R^2 = 0.850) fitted the Freundlich model (Table 4-8). These models are suitable to model pure or mono component systems, whereas the wastewater used to complete this study was high strength multi-component wastewater that contained many pesticides. As a result, this makes it difficult to adjust the models but presented the affinity of the adsorber for the system in the presence of a complex matrix.

When looking at the Langmuir model it can be seen that 2,4-DCP and PCOC had significantly higher saturation capacities (qm) at 1667 and 137 when compared with MCPA, MCPP and 2,4-DB, 14, 3.4 and 9.8, respectively. All compounds had a low affinity for the adsorbent with the highest value of 0.415 for 2,4-DB. As expected the pesticide production wastewater does not fit Langmuir adsorption model particularly well. This is because the Langmuir model assumes that every molecule has equal affinity and the coverage level does not impact on affinity. The model also assumes a mono-layer coverage with a fixed number of sites and reversible adsorption. The model assumes that the pesticides are single components in the wastewater. However the pesticide production wastewater is a very complex matrix and it has multi-compounds (Hameed et al., 2009; Jusoh et al., 2011).

When evaluating the Freundlich model the results show that only MCPA and MCPP were suitable for GAC adsorption with K values of 0.713 mg/g and 0.963 mg/g, respectively. However these values obtained are just relative and give an indication of affinity/selectivity, they are not absolute because of the complexity of the system, as previously discussed. It is recommended in literature that K values over 0.2 mg/g are suitable for GAC adsorption. Intensity of adsorption by adsorbate showed that MCPP had the highest adsorption strength (9.2). The Freundlich model also assumes every molecule has equal affinity and that the coverage level does not impact on affinity, hence it is more suitable to describe single component adsorption (Jusoh et al., 2011).

Table 4-8. Freundlich and Langmuir models.

	Langmuir			Freundlich		
Compounds	**R^2**	**1/qm**	**b**	**K**	**1/n**	**R^2**
2,4-D	-	-	-	-	-	-
MCPA	0.964	14.0	0.035	0.7	5.2	0.937
PCOC	0.714	137	0.025	-0.2	0.6	0.699
2,4-DCP	0.826	1667	0.002	0.1	1.2	0.850
2,4-DP	-	-	-	-	-	-
MCPP	0.630	3.4	0.178	1.0	9.2	0.752
2,4,6-TCP	-	-	-	-	-	-
2,4-DB	0.535	9.79	0.415	0.2	1.5	0.428
MCPB	-	-	-	-	-	-

qm - Saturation capacity
b - Affinity of the adsorbate for the adsorbent
K- Capacity of adsorbent
1/n -Intensity of adsorption
R^2 – correlation coefficient

Biochar showed significantly lower adsorption capacities between 8-18 fold for the target pesticides when compared to F-400 GAC (Figure 4-6 and Table 4-9). This could be due to the fact that the biochar used in these experiments was not activated. Activation of carbon creates more micropores for the adsorption to take place. Table 4-9 compares the capacity of standard biochar (average particle size 501 µm) and biochar with increased surface area (average particle size 53-63 µm). The aim of grinding the biochar was to obtain smaller particles and increase the surface area per volume. Results showed no benefit of grinding the biochar to smaller particles. It seems that grinding only increased the surface area and not number of pores whereas activating the carbon would have been more beneficially as activation creates more micropores for the adsorption to take place.

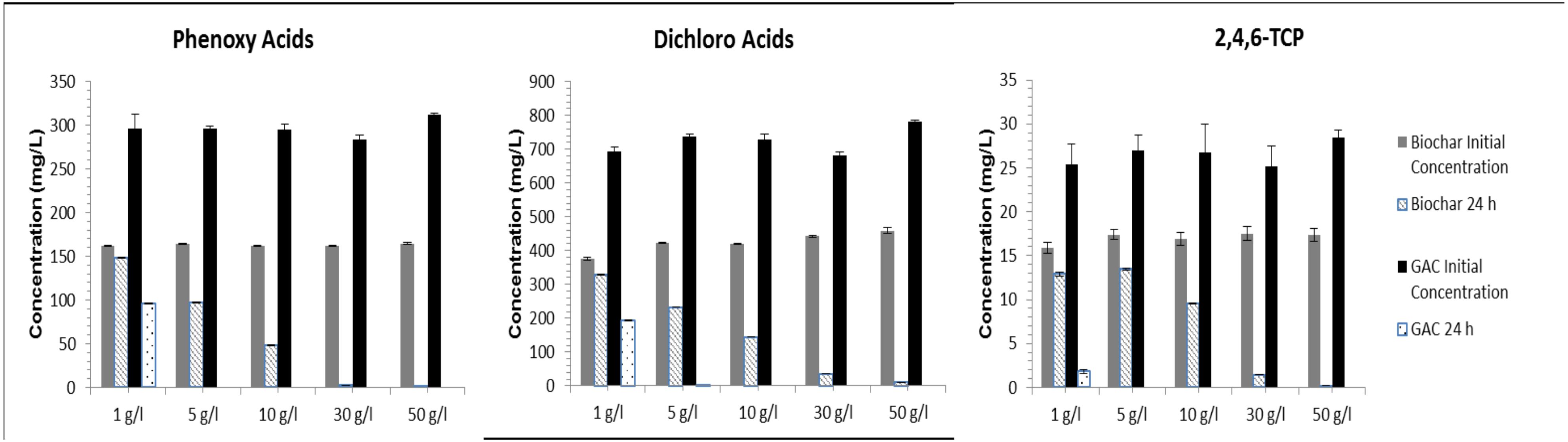

Figure 4-6. Synthetic pesticide solution removal in batch tests with same initial pesticide concentrations over 24 hours for phenoxy acids (MCPB, MCPA, PCOC, MCPP), dichloro acids (2,4-D, 2,4-DP, 2,4-DB, 2,4DCP) and 2,4,6-TCP. Tests were completed with GAC dosed at 1-50 g/L.

Table 4-9. Comparison between standard biochar and biochar with increased surface area capacity at different doses when using synthetic pesticide solution.

		Adsorber concentration (g/L)														
		1			5			10			30			50		
	Compounds	GAC	Biochar	Biochar with Increase surface area	GAC	Biochar	Biochar with Increase surface area	GAC	Biochar	Biochar with Increase surface area	GAC	Biochar	Biochar with Increase surface area	GAC	Biochar	Biochar with Increase surface area
Capacity (q) (mg/g)	**MCPA**	39.10	2.26	3.72	>7.74	0.49	0.61	>3.93	0.68	0.45	>1.28	0.58	0.44	>0.82	0.37	0.35
	PCOC	132.26	11.37	2.68	>45.35	12.54	8.89	>22.87	10.18	7.76	>7.31	4.43	3.76	>4.80	2.71	2.34
	2,4-DCP	472.27	50.54	31.83	142.26	35.92	24.75	>70.50	24.89	15.57	>21.95	12.39	7.23	>15.08	8.24	3.94
	2,4-DP	>10.21	0.61	-0.05	>1.75	0.27	0.00	>0.90	0.27	0.08	>0.25	0.15	0.09	>0.21	>0.09	0.05
	MCPP	>17.75	0.00	0.27	>3.28	0.26	0.28	>1.68	0.45	0.25	>0.51	0.32	0.22	>0.37	>0.2	0.17
	2,4,6-TCP	23.59	2.97	0.76	>5.39	0.79	0.22	>2.67	0.73	0.21	>0.84	0.54	0.24	>0.57	0.34	0.16
	2,4-DB	>16.33	0.00	0.00	>3.60	1.84	0.20	>1.44	2.35	1.28	>0.49	1.00	0.82	>0.32	0.64	0.52
	MCPB	>11.28	0.02	0.13	>2.90	0.01	0.02	>1.00	0.01	0.01	>0.35	>0.01	0.02	>0.25	>0.00	0.00

[redacted] Column experiments using GAC

Figure 4-7 shows the breakthrough of pesticides present in the pesticide production wastewater at 3, 5, 10 and 30 minutes empty bed contact time (EBCT). Breakthrough was assumed when the pesticides concentration was the same in the effluent as in the influent. At 3 minutes EBCT, the first pesticide broke through at 599 bed volumes (BV) (2,4-DB), at 5 minutes EBCT the first pesticide broke through at 624 BV (MCPA), at 10 minutes EBCT the first pesticide broke through at 1020 BV (MCPB) and at 30 minutes EBCT the first pesticide broke through at 1374 BV (MCPA). These tests were completed with different pesticide production wastewater batches, collected at different times. Hence some variability of compounds reaching breakthrough was anticipated due to variable wastewater quality.

Typical EBCTs for industrial wastewater treatment is in the range of 30-540 minutes (Hung et al., 2005). These low EBCTs tested in this study allowed a larger volume of wastewater to be treated at one time when compared to the typical EBCTs, however longer EBCTs should be tested for this pesticide wastewater. Knappe et al. (1997) found when treating pesticide atrazine using GAC at 8.4 and 8.6 minutes EBCTs, regeneration of the GAC was required between 5-20 months. However the initial concentrations were much lower (3.7-4.1 µg/L) than the wastewater used in this study.

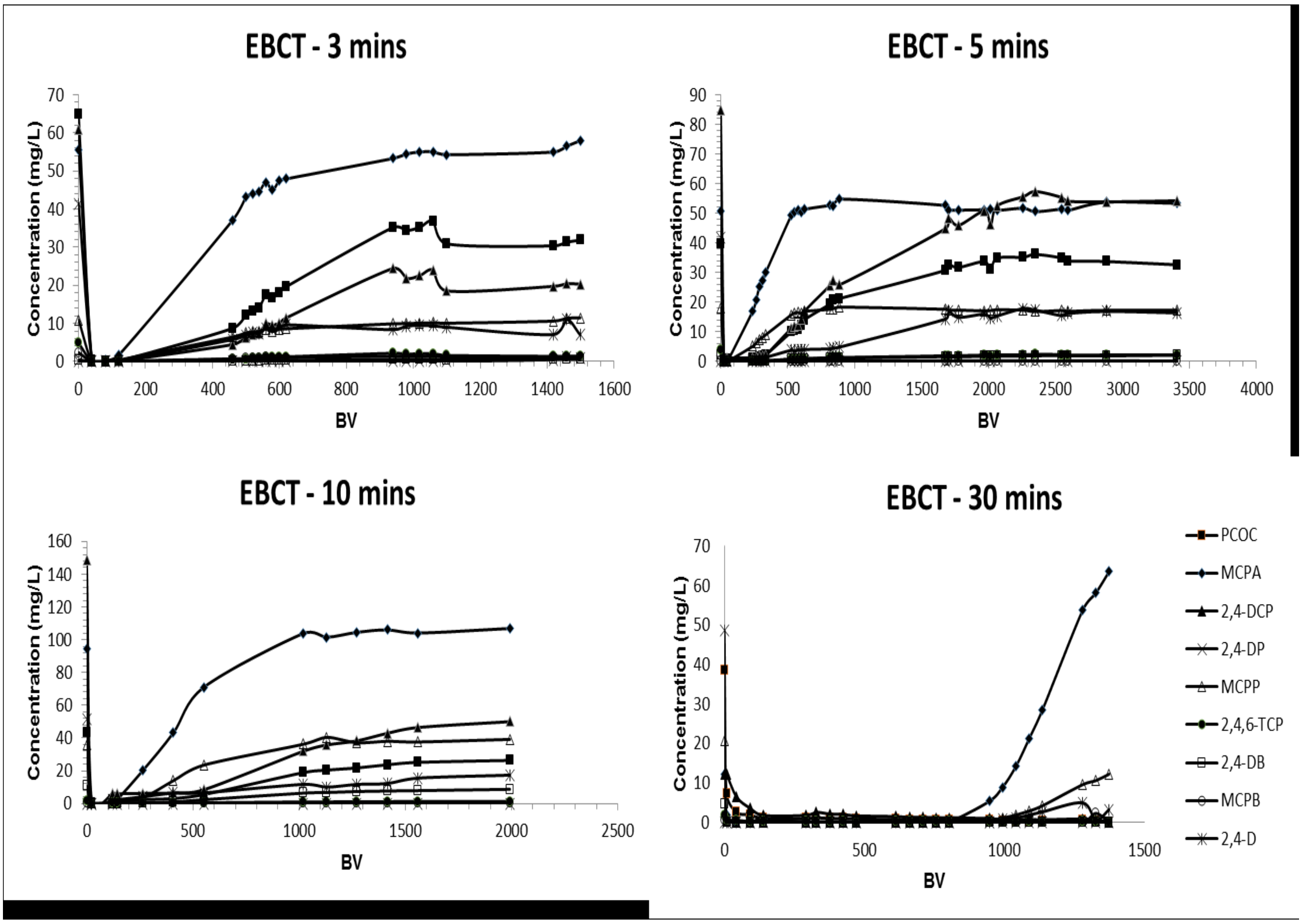

Figure 4-7. Breakthrough curves in column experiments using GAC F-400 continuously fed with pesticide production wastewater.

The capacity of the GAC and length of unused bed was obtained from the breakthrough curves for the corresponding pesticide that reached breakthrough first. Table 4-10 shows the length of unused bed for the different EBCTs (3,5,10 and 30 minutes). The results show that the length of unused GAC bed decreases with higher EBCTs, 3 and 10 minutes EBCTs had H_{UNB} 2.6 and 0.03 cm, respectively. When comparing 5 and 30 minutes EBCT, both experiment had MCPA breakthrough first. The results suggest that increasing the EBCT increases the capacity of the GAC for MCPA from 42 mg/g to 200 mg/g. therefore increasing the EBCT would mean regeneration of the GAC media would be less frequent (Knappe et al., 1997).

Table 4-10. GAC F-400 length of unused media, breakthrough and saturation capacities for real pesticide production wastewater completed in continuous column experiments.

	EBCT (minutes)			
	3	5	10	30
H_{UNB} (cm)	2.6	1.5	0.03	-
q (mg/g)	0.40	42	0.29	199.9
q* (mg/g)	0.73	56.5	0.57	-
Pesticide to breakthrough	2,4-DB	MCPA	MCPB	MCPA

Where, H_{UNB} - length of unused GAC bed, q – capacity used, q* - saturation capacity

4.4.4 Chemical process test with AOPs

[redacted] Fenton process

Figure 4-8 shows the initial and final concentrations of pesticides in synthetic and pesticide production wastewater after being in contact with various doses of H_2O_2 and Fe^{2+}. Fenton process showed no removal of pesticides present in the pesticide production wastewater when using 100-1250 mg/L H_2O_2 and 5-20 mg/L Fe^{2+} (Figure 4-8 top). Similar conditions were used in other studies reported in the literature using low concentrations of hydrogen peroxide (100 mg/L) (Ma et al., 2009; Zapata et al., 2009) but higher of Fe at 20 mg/L (Zapata et al., 2009).

Further tests were completed with 12500 mg/L of H_2O_2, but negligible pesticide removal were obtained (Figure 4-8 top). Removal levels between 90-100% have been observed when using Fenton process to treat organochlorine pesticides in industrial wastewater at concentration up to 377 µg/L with a 5000 µg/L H_2O_2 (Barbusiński et al., 2001). The wastewater investigated in this study had a significantly higher pesticide concentration and with a complex matrix with high COD and BOD concentrations 33750 and 11590 mg/L, respectively. Organic matter and alkalinity can act as radical scavengers, leading to low effectiveness of the Fenton process, potentially explaining the results here obtained.

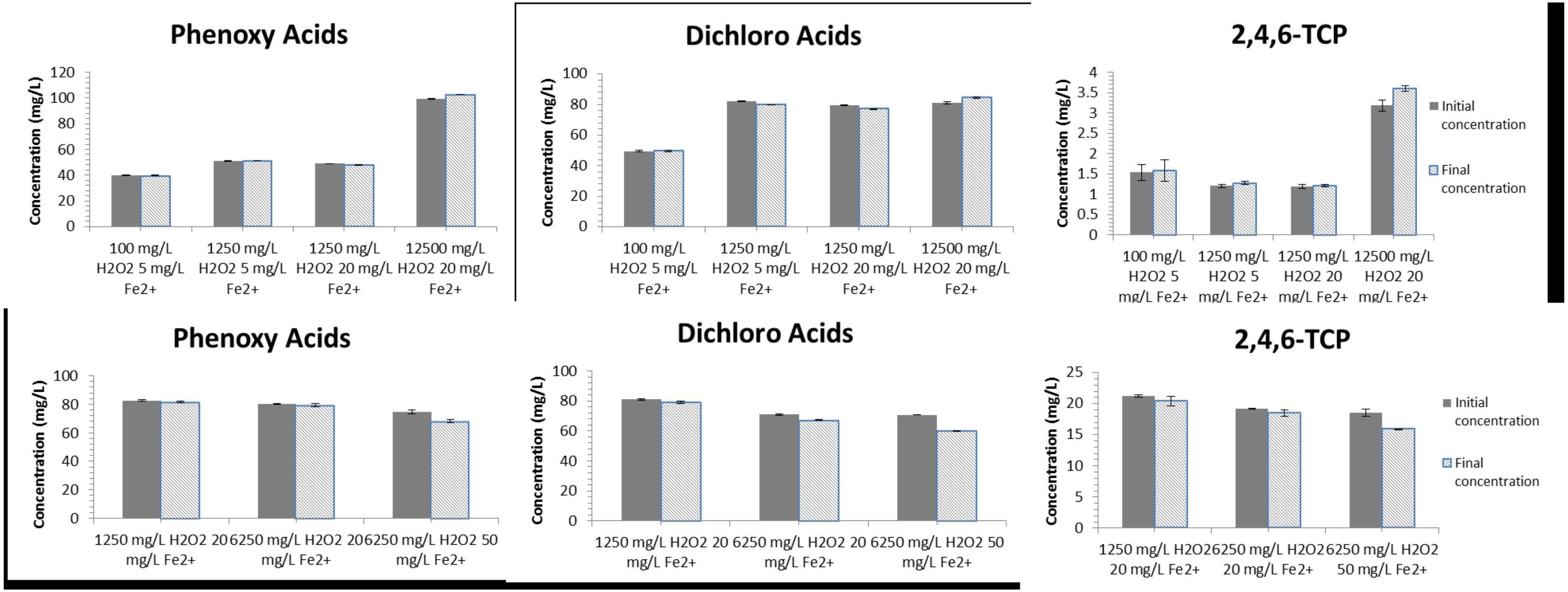

Figure 4-8. Initial and final concentration of pesticides in pesticide production wastewater (top) and synthetic pesticide solution (bottom) after treatment with Fenton process at various doses of H2O2 and Fe2+. Phenoxy acids include MCPA, PCOC, MCPP and MCPB and dichloro acids include 2,4-D, 2,4-DP and 2,4-DB.

To further investigate the results, synthetic pesticide solutions were used to isolate the effect of water matrix. The initial concentration of each pesticide was 25 mg/L and tests were completed with a combination of H_2O_2 and Fe^{2+} doses (Figure 4-8 bottom). At 1250 mg/L H_2O_2, the pesticides remained at a similar concentration to the initial concentrations with total pesticide removals at 2%. At 6250 mg/L H_2O_2, the total pesticide removal was at 3%. By increasing Fe^{2+} concentration from 20 mg/L to 50 mg/L the total pesticide removal was 12%. Showing that increasing Fe^{2+} increased the pesticide removal. This shows that the matrix of the pesticide wastewater had no effect on the treatment process and large chemical concentrations were required to treat this wastewater. Barbusiński et al. (2001) studied removal of organochloride pesticides in industrial wastewater and succesfully achieved a removal between 90-100% using 5 g/L Fe^{2+} but with initial pesticide concentrations up to 0.38 mg/L. In this study the high concentration of pesticides (0.12-59 mg/L) would result in high Fe^{2+} concentration in the wastewater that would need to be removed before been safely discharged. Also using high Fe^{2+} concentration would require the pH to be adjusted twice, once to acidify for the Fenton process to work and another adjustment to increase pH to precipitate the Fe^{2+} and remove it from the wastewater. This would be an expensive treatment option as high Fe^{2+} doses would generate high operational expenditure (OPEX) and increase sludge production.

In the tests with synthetic pesticide solution and high doses of H_2O_2 (6250 mg/L) and Fe^{2+} (50 mg/L) the total pesticides removal was 12%. Equation 4-6 and 4-7 show the reactions that occurred during the process. Radicals are generated utilising iron as a catalyst and hydrogen peroxide as an oxidant. Throughout the process iron is cyclically reduced and oxidised in a redox cycle. Oxidation occurs in equation 4-6, a fast reaction whilst equation 4-7 is a much slower. In equation 4-7 no hydroxyl radicals are produced but Fe^{2+} production is required as a reagent for equation 4-6. Since increasing Fe^{2+} concentration improved the pesticide removal, this proves that equation 4-7 is limiting the process.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\bullet \quad \textbf{(Equation 4-6})$$

$Fe^{3+} + H_2O_2 \rightarrow H^+ + HOO\bullet + Fe^{2+}$ **(Equation 4-7)**

This effect has been previously reported in the literature (Carra *et al.*, 2014, 2015). The addition of UV-Vis ($\lambda<600$ nm) (photo-Fenton process) would overcome this problem as the reduction of ferric iron would take place equation 4-8, which is faster than reaction than equation 4-7 and in addition generates hydroxyl radicals. However, this technology has yet to be developed and there are no commercially available UV-based photoreactors for this process.

$Fe^{3+} + H_2O + hv \rightarrow HO\bullet + H^+ + Fe^{2+}$ (**Equation 4-8)**

[redacted] UV/H_2O_2 experiments

The application of UV/H_2O_2 process consists of adding hydrogen peroxide to generate radicals and remove organic pollutants. The results showed total pesticide removal (phenoxy acids, dichloro acids and 2,4,6-TCP) were 49% with just UV, 40% with UV/H_2O_2 1250 mg/L and 32% with UV/H_2O_2 6250 mg/L (Figure 4-9). It was thought increasing the concentration of H_2O_2 would increase the number of hydroxyl radicals generated and therefore increase pesticide removal. However from the results shown (Figure 4-9 and Appendix A), UV photolysis was a shown to be efficient at removing the pesticides without the presence of H_2O_2 (Figure 4-9). This is due to the compounds been able to absorb UV light and photolyse at 254 nm. The results suggests adding H_2O_2 acts like a barrier and reduces the amount of UV light making contact with the pesticides and therefore lowers pesticide removals levels. This is supported by increasing the H_2O_2 concentration to 6250 mg/L as pesticide removal levels are further reduced. James et al. (2014) studied 2,4-D and MCPP. Results showed that using a 3 mg/L dose H_2O_2 with an intensity of 0.62 Kwh/m^3, 2,4-D and MCPP could be removal 89% and 98%, respectively, however these results could not be repliacted in this study

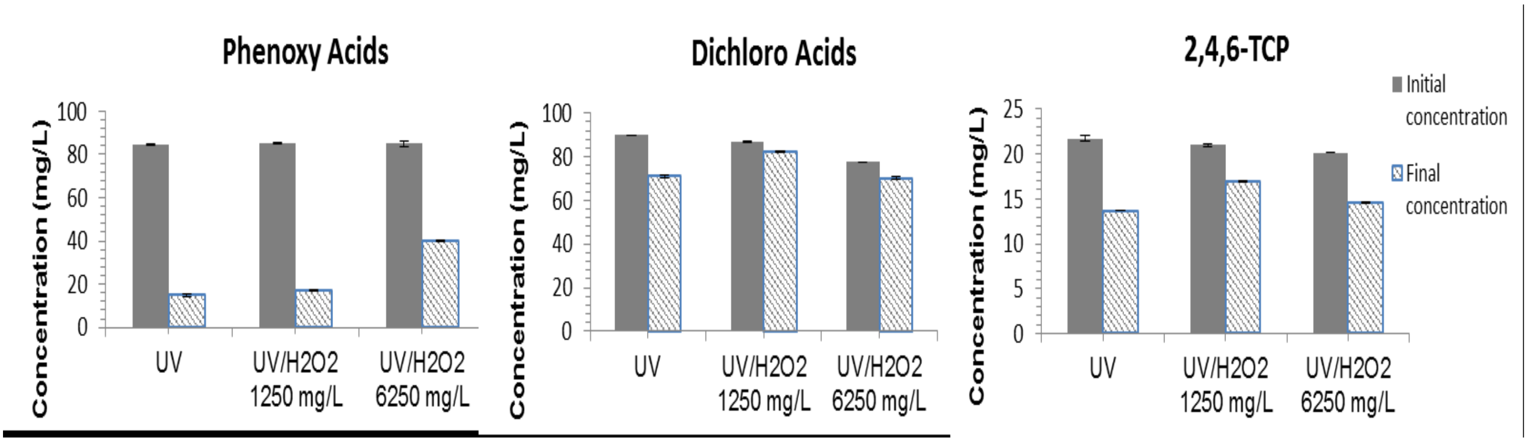

Figure 4-9. Initial and final concentration of pesticides after treatment with UV and UV/ H2O2 in synthetic pesticide solutions at 3 mW/cm2. Phenoxy acids include MCPA, PCOC, MCPP and MCPB and dichloro acids include 2,4-D, 2,4-DP and 2,4-DB.

4.5 Conclusion

Biodegradation of pesticides in the production wastewater was achieved for phenoxy acids (MCPA, MCPB, MCPP and PCOC) and 2,4,6-TCP at a 25% wastewater dilution. At this concentration there was no toxicity and removal efficiencies were 37% and 30%, respectively. Removals for dichloro acids (2,4-D, 2,4-DB, 2,4-DP and 2,4-DCP) were -64% due to the accumulation of 2,4-DB. Dosing additional nutrients alkalinity was found to improve the biological activity. Acclimatisation studies were inconclusive Anaerobic biodegradability tests showed that the wastewater was toxic to anaerobic digested sludge microorganisms up to 1% dilution of the wastewater.

Batch tests using GAC showed good adsorption of pesticides. The equilibrium times were around 5 hours and 58-100% pesticide removal was observed within 24 hours. Column tests carried out showed breakthrough occurred between 599-1374 bed volumes when using 3-30 minutes EBCT, suggesting that longer EBCTs experiments should be tested. Overall, the GAC experiments demonstrated this treatment option can efficient and reliable option for treating this pesticide production wastewater.

Results revealed that AOPs (Fenton process and UV/H_2O_2) were not suitable for treating this specific pesticide production wastewater. Studies carried out show that adding H_2O_2 reduces the pesticide removal levels by filtering the UV light. It is clear that the pesticides in this study are able to be degraded with total pesticide removal of 50% by utilising UV alone at an intensity of 30 W/m^3.

4.6 References

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▌Removal of phenoxy acids and dichloro acids from a pesticide production wastewater using hybrid systems

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5.1 Abstract

A combination of processes (granular activated carbon, membrane bioreactor and ultraviolet photolysis) were investigated for their ability to remove 9 pesticides (phenoxy acids and dichloro acids) from a high strength industrial wastewater from the pesticide production industry. A lab-scale hybrid system composed by granular activated carbon (GAC) continuous columns followed by an aerobic biological process achieved total pesticides removal of 89%. A pilot scale membrane bioreactor (MBR)-GAC hybrid system was also tested. After diluting the wastewater to 25%, to prevent toxicity to the MBR process, the chemical oxygen demand (COD), biological oxygen demand (BOD) and total pesticides removal efficiencies were 71, 50 and 83-99%, respectively. Adding nutrients and alkalinity to the MBR increased carbon and pollutants removal (COD 88%, BOD 72% and pesticides 86-99%). Photolysis with UV showed promising results to replace the GAC, as the MBR-UV system achieved a total pesticides removal of to 98-99%. This study demonstrates the benefits and feasibility of utilising different configurations of hybrid systems including MBR and GAC and UV to treat high strength pesticide production wastewater.

5.2 Introduction

Pesticide application has many benefits such as crop disease control and protection, food preservation, to name a few (Aksu and Kabasakal, 2004; Oller et al., 2011). Pesticide production worldwide reached 2.3 million tons in 2007 with herbicides accounting for 40% of the market (Grube *et al.*, 2011). Although pesticides are one of the most widely used group of chemicals worldwide, they are also amongst the most threatening to environmental and human health due to effects such as toxicity, carcinogenicity and bioaccumulation in living organisms (Benfeito *et al.*, 2014).

Herbicides are manufactured in industrial facilities with formulations containing active compounds such as bipyridyls, glyphosate, glyphosate, acetanilides, triazines and chlorophenoxy. The later are used to control weeds in a wide range of agricultural crops as well as in non-agricultural areas (e.g.: brush control), control of aquatic weeds, and in orchards as pre-harvest treatment (Benfeito *et al.*, 2014). Chlorophenoxy herbicides are easily transported in water systems (surface and ground waters) due to their relatively high solubility and polar nature, and hence their uncontrolled discharge can lead to severe environmental contamination and damage. Consequently, the control and suitable treatment of wastewater originating from pesticide production industry is critical to ensure environmental protection. Chlorophenoxy herbicides production wastewater is typically a medium to very high strength complex wastewater containing many toxic compounds capable of causing toxic effects in the environment (Kim *et al.*, 2008). Pollutants such as 2,4, dichlorphenoxy acetic acid (2,4-D); 2,4 dichlorophenol (2,4-DCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA); mecoprop (MCPP); toluene and xylene are classified as priority substances according to the Water Framework Directive (WFD) (European Commission, 2008). Environmental quality standards (EQS) for these compounds are 0.3 μg/L (2,4-D), 20 μg/L (2,4-DCP), 18 μg/L (MCPP) and 2 μg/L (MCPA) therefore effective removal of pesticides at wastewater treatment plants (WWTP) is crucial in order to achieve the required limits.

Pesticide production wastewater is typically treated using combination of processes such as coagulation, filtration, and biological processes (e.g. conventional activated sludge process and trickling filters) (Mcallister *et al.*, 1993; Bernhard, Muller and Knepper, 2006; Soares, 2015). Conversely, these processes do not provide reliable effective treatment for pesticide removal as many studies have reported biological processes to be challenging when treating such wastewaters due to pollutants showing toxicity towards microorganisms and strong recalcitrance (Jin *et al.*, 2010; Oller et al., 2011). This presents uncertainty whether these processes have the ability to achieve the required EQS limits.

The use of membrane bioreactor (MBR) systems over conventional activated sludge process (ASP) is increasing due to many studies reporting enhanced effluent quality. MBR systems have been used to treat domestic wastewater at various scales but over the last decades MBRs have been developed and used for industrial wastewater treatment including pesticides and pharmaceuticals (Lim et al, 2004). Membrane bioreactors are intensive activated sludge processes in which the final settler is substituted by ultra-filtration or micro-filtration membranes, which retains all suspended solids (SS) therefore producing a high quality effluent (Cirja *et al.*, 2008). When treating high strength industrial wastewater shock loads might occur, for this reason MBRs are commonly used as they allow for complete retention of microbial biomass, enhancing process resilience (Mutamim et al. 2013). Other advantages of using MBRs in comparison with ASP include a 30-50% reduction in footprint, simple process operation, low sludge production and high effluent quality (Cirja *et al.*, 2008). Membrane bioreactors eliminate all suspended solids and pathogens from the effluent, whilst standard ASP systems will require an additional tertiary processes to achieve the same effluent quality (Haandel et al. 2011). Furthermore ASP operate at 1-7 g/l mixed liquor suspended solids (MLSS), whilst the MBR operates significantly higher MLSS between 7-25 g/l, allowing for higher reaction rates and resilience (Cirja *et al.*, 2008). The long sludge retention times (SRT) in MBRs (between 25-150 days compared to conventional ASP at 3-25 days) allows for sludge hydrolysis, reducing its production and enhanced pollutant removal (Stephenson et al. 2000; Göbel et al. 2007; Radjenović et al. 2009; Cirja et al. 2008). The sludge retained in the MBR can adsorb pollutants enhancing microbial degradation (Spring et al, 2007). On the other side, MBRs are more expensive to operate than ASP due to a higher energy demand (high MLSS concentration demands a high oxygen supply), but also membrane fouling is controlled by intense aeration and membrane needs replacing every 5-10 years, depending on the type of wastewater.

Bernhard et al. (2006) utilized a submerged lab-scale MBR to study the fate of a number of persistent pollutants including MCPP. The pH ranged between 6.6- 7.8 and the MBR was operated with an HRT of 7 - 10h. The MCPP removal was between 36 - 64% from an initial concentration of <23 µg/L (Bernhard et al., 2006). In a pilot-plant MBR the removals of 2,4-dichlorophenoxyacetic acid (2,4-D), methyl-chlorophenoxypropionic acid (mecoprop), and 3,6-dichloro- 2-methoxybenzoic acid (dicamba) (at concentrations from 300 µg/L to 3.5 mg/L) were 99, 69.0 and 75.4%, respectively (Ghoshdastidar and Tong, 2013). Both these studies report the use of

MBRs for treatment of low pesticide concentrations. The MBR process efficiency for high strength and high concentration of pesticides (in the order of mg/L) is still not yet understood.

On the other side, the US Environmental Protection Agency (EPA) recommends granular activated carbon (GAC) as the best available technology (BAT) for organic compound removal due to its high efficiency for removing a wide range of organic compounds including pesticides (Evoqua Water Technologies, 2016). Studies show when utilising GAC as a pre-treatment process the adsorption of pesticides is decreased due to high competition with other bulk organic matter for adsorption pores. This can lead to reduced lifespan and increased frequency of media regeneration, which makes the process very expensive (Nguyen *et al.*, 2012). Literature suggests using GAC as a post-treatment to increase adsorption of pesticides. This entails that most of the bulk organic matter must be removed prior to using GAC columns (Nguyen *et al.*, 2012).

The use of UV photolysis has been used to remove recalcitrant pollutants in wastewater by either UV alone or more commonly combined with hydrogen peroxide or ozone (Kowalska *et al.*, 2004; Lafi and Al-Qodah, 2006). Application of UV alone is not used often due to it being a slow process efficient only with compounds absorbing light at the emitted wavelength of the lamp. When combined with hydrogen peroxide or ozone the rate at which hydroxyl radicals are generated is greatly increased allowing the oxidation of pollutants to happen much faster. Other substances can be added such as catalysts such as titanium dioxide (TiO_2), this also helps to increase the creation of hydroxyl radicals (Irmak et al., 2004; Oller et al., 2011). This treatment process is currently not been used at large scale, but studies have been carried out at bench/pilot scale work which would be easily scalable.

In this study GAC and UV photolysis were combined with aerobic biological processes in order to investigate their ability to remove 9 pesticides (phenoxy acids and dichloro acids including 2,4-dichlorphenoxy acetic acid (2,4-D); 4-(2,4-dichlorphenox) propionic acid (2,4-DP); 4-(2,4-dichlorophenox) butyric acid (2,4-DB); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-

methylphenoxy) butyric acid (MCPB) and 2-(4-chloro-2-methylphenoxy) propionic acid (MCPP) from a high strength industrial wastewater from the pesticide production industry and reach the EQS set by the Water Framework Directive (WFD) (European Commission, 2008).

5.3 Materials and Methods

5.3.1 Materials and calibration standards

The chemicals 2,4-D (99+%), 2,4-DCP (99%), 2,4-DP (98%), 2,4,6-TCP (98%) and PCOC (97%), iron sulphate, hydrogen peroxide (30%) ammonium chloride, sodium phosphate and sodium carbonate were purchased from Fisher Scientific (UK), 2,4-DB was purchased from VWR (UK) and MCPA (100%), MCPB (100%), MCPP (100%), internal standard (IS) 2,3,4,5-tetrachlorophenol (2000 µg/ml), surrogate standard (SS) 2,4-dichlorophenylacetic acid (2,4-DCAA 100 µg/ml) and trimethylphenylammonium hydroxide (TMPH) solution at 0.2 M solution in methanol were purchased from Sigma-Aldrich (Germany). Granular activated carbon F-400 with a particle size in the range of 500 µm–1 mm was purchased from Envirochem (UK). All solvents were high performance liquid chromatography (HPLC) grade or gas chromatography-mass spectrometry (GC-MS) and ultra-pure deionised water was obtained from Milli-Q (Purelab, Elga, High Wycombe, UK).

A stock solution containing 2,4-D, 2,4-DP, 2,4-DB, 2,4-DCP, 2,4,6-TCP, PCOC, MCPA, MCPB and MCPP 100 mg/L in methyl-tert-butyl ether (MTBE) was used to create calibration standards for the GC-MS. Each standard contained a total volume of 1.52 ml containing 1 ml pesticide solution (containing the additional surrogate standard), 0.5 ml derivatisation reagent (TMPH) and 0.02 ml internal standard.

5.3.2 Wastewater and activated sludge seed

The pesticide production wastewater was sourced from industrial facility producing a range of commercial herbicides in the UK. Samples of the pesticide production wastewater for the various tests were collected at regular intervals and quality of the wastewater varied according to the different formulations produced at the facility. Activated sludge, for seeding the biological process and MBR, was sourced from a full scale WWTP with a 760,000 population equivalent treating domestic wastewater.

5.3.3 Operation procedure for GAC – Biological hybrid system

A lab scale hybrid process using GAC as a pre-treatment combined with a biological process was set up (Figure 5-1). The continuous flow GAC column experiments were conducted in glass columns (length 41 cm and 3 cm internal diameter), containing 7.5 g (10 ml volume) F-400 GAC media. Prior to the experiment the GAC was sieved and washed with deionised water and ethanol to prevent voids, cracks and channels. The column was loaded with wastewater at a constant flow of 1 ml/min in order to achieve the specific empty bed contact time (EBCT) of 10 minutes. All experiments were carried out at room temperature. Samples were collected at regular intervals throughout the duration of the experiments and filtered before analysed on the HPLC to quantify the pesticide removal.

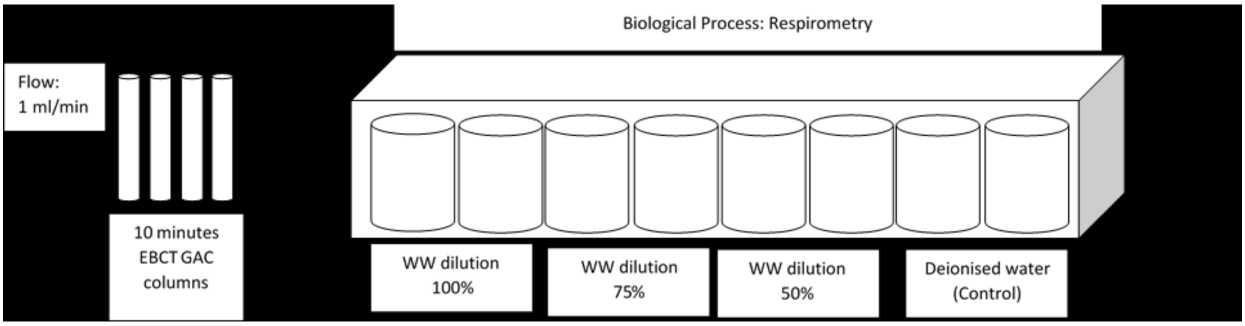

Figure 5-1. Schematic representation of the lab-scale GAC columns and biological process (respirometer) hybrid system.

The biological process was completed using a manometric respirometer (Environmental Services Ltd, Cornwall, UK) as described by Raper et al (2017) to assess the oxygen uptake rate of the activated sludge (AS) biomass and evaluate the toxicity of pesticide production wastewater. The test bottles were inoculated with AS with a MLSS concentration approximately 7000 mg/L (to mimic the conditions of long SRT ASP or an MBR) and effluent from the GAC columns at various dilutions 100%, 75% and 50%. The control experiments were prepared the same way, but the GAC effluent was replaced with dionised water. All tests were carried out in duplicate and run for 48 hours. Samples were filtered before analysed on the HPLC to quantify the pesticide removal.

5.3.4 Operation procedure for MBR – GAC - UV hybrid system

A combination of hybrid systems consisting of pilot-plant MBR followed by GAC continuous column tests and UV photolysis were set-up (System 1: MBR + GAC; System 2: MBR+GAC+UV and System 3: MBR+UV) (Figure 5-2). The MBR consisted of full-scale polyvinylidene difluoride (PVDF) hollow fibre membrane module (26 cm dimeter, 160 cm long, and a 0.04 µm pore size) with an effective membrane surface area of 0.233 m^2 submerged in a 42.5 L tank with a working volume of 30 L. The MBR was operated at a 16 hours hydraulic retention time (HRT) and flux of 8 $L/m^2.h$ (LMH), according to previous studies treating industrial wastewater (Bernhard et al, 2006; Göbel *et al.*, 2007; Ghoshdastidar *et al.*, 2015). The flow regime used 9 minutes pumping and 1 minute relaxing/off. The temperature of the MBR system was 14^oC± 2^oC and monitored using a temperature probe. The aeration rate was 1400 L/hour to ensure aerobic conditions. The MBR tank was inoculated with AS from a full-scale WWTP with a MLSS concentration approximately 7000 mg/L. Pesticide production wastewater was diluted to 25%, as it was previously shown that this dilution prevents toxicity towards AS microorganisms (as demonstrated in this thesis chapter 4). Dilution was achieved by pumping the pesticide production wastewater and tap water to an in-line static mixer (Colm Parmer, UK) prior to been pumped into the MBR at a controlled flow rate of 1.9 L/h. After 7 days of operation, nutrients; ammonium chloride (NH_4 - 1.7 g/L), monosodium dihydrate phosphate (PO_4 – 0.23 g/L), and alkalinity; calcium carbonate (100 mg/L) were dosed to the wastewater, according to previous results (as demonstrated in this thesis chapter 4). Samples were collected 2 times per week for pesticide analysis via HPLC and chemical oxygen demand (COD), biological oxygen demand (BOD) analysis.

Effluent was then pumped to continuous flow GAC columns. The glass columns (length 41 cm and 3 cm internal diameter), contained 15 and 30 g (20 ml and 40 ml volume) of F-400 GAC. Prior to the experiment the GAC was sieved and washed with deionised water and ethanol to achieve a closely packed arrangement of particles without voids, cracks and channels. The GAC columns were loaded with the effluent from MBR at a constant flow of 0.66 ml/min in order to achieve 30 and 60 minutes EBCT. Samples were collected 2 times per week to measure COD and BOD as well as quantify pesticide removal using GC-MS analysis.

Effluents from the MBR and GAC columns was transferred to a 250 ml reactor and exposed to UV light (intensity of 3 mW/cm^2) to investigate pesticide photolysis. All experiments were conducted in a Wedeco AG bench scale quasi-collimated beam apparatus (Herford, Germany) equipped with four 30 W UV-C low pressure lamps which emits a monochromatic light a wavelength of 254 nm. Samples were mixed using a stirrer plate at room temperature, 20°C and carried out in a dark room. Samples were taken over a period of 1 hour and filtered through a 0.45 µm syringe filter (Millex-HA). The reaction was stopped before the pesticides being quantified on the HPLC by using acetonitrile as a quenching agent since it acts as a radical scavenger.

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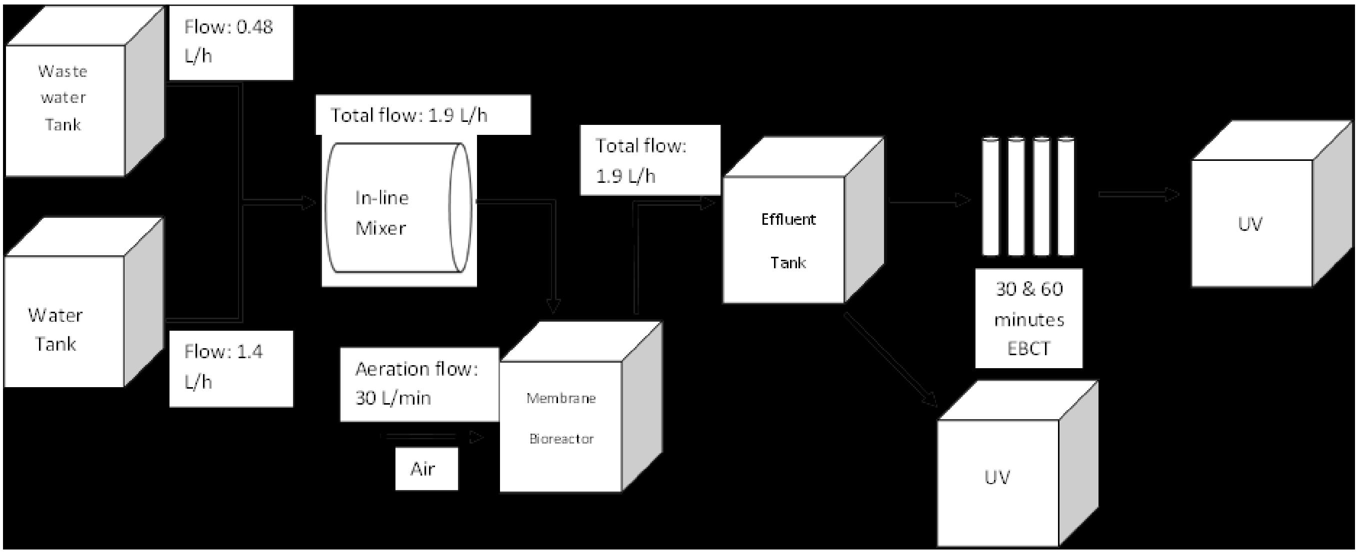


Figure 5-2. Schematic representation of the pilot scale pesticide production wastewater system: System 1: MBR + GAC; System 2: MBR+GAC+UV and System 3: MBR+UV.

5.3.5 Analysis

[redacted] Wastewater characterisation

Wastewater samples were analysed for COD, NH_4, PO_4 using cell tests according to the manufacture standards (Merck, Millipore). Biochemical oxygen demand, total suspended solids (TSS), volatile suspended solids (VSS), Alkalinity were measured according to standard methods (Eaton, 2005). The pH of the wastewater samples were monitored using a calibrated pH probe.

[redacted] HPLC

The pesticides were quantified using a Shimadzu DGU-20A5 (Shimadzu, Japan) HPLC equipped with a UV detector (series SPD-20A) with the columns Fortis Cyano 250 mm x 4.6 mm, 5µm column (Chromex Scientific, UK) and a corresponding 2 cm cartridge guard column (Chromex Scientific, UK). The mobile phase consisted of 70% deionised water and 30% acetonitrile + 0.4% acetic acid at a flow rate and sample injection volume of 1 ml/min and 50 µl, respectively. The detector was set at 280 nm, the column temperature was set to 20ºC and the analysis ran for 25 minutes.

[redacted] GC-MS

Hundred millilitres wastewater samples were acidified with hydrochloric acid (1M) to pH 3 and spiked with 1250 µl SS were loaded onto the cartridges (Sep-Pak Vac 6cc (500 mg) tC18 cartridges (Waters) at a loading rate of 1 ml/min. The cartridges were previously conditioned with methyl-tert-butyl ether (MTBE) (1x3 ml), methanol (2x3 ml) followed by acidified deionised water pH 3 (1x3 ml). During the extraction process the cartridges were not allowed to dry out. Acidified deionised water (3 ml) was used to wash the cartridges before drying using a gentle stream of air. The pesticides were eluted with MTBE (5 ml), and evaporated to dryness in a test tube under a gentle stream of nitrogen. One millilitre MTBE was added to the test tube and vortex to re-suspend the pesticides before transferred to a GC-MS vial. Derivatisation reagent (TMPH) was added to the vials at a 20 times mass molar excess (0.5 ml) and 20 µl IS was spiked and mixed in the sample. In addition to samples, a blank and a standard were included to check quality control. The pesticides in the extracted samples were detected and quantified using a GC-MS (Agilent) with an Rtx-5MS fused silica column (30 m x 0.25 mm x 0.25 µm). The working parameters for the GC-MS were as follows: injection volume 1µl; injector temperature 250°C; injection system splitless; carrier gas helium at 1 ml/min; oven temperature program 80 °C - 6 °C/min - 200 °C – 30 °C/min - 280 °C – 5 min and detector temperature 320 °C.

5.4 Results and Discussion

5.4.1 Pesticide production wastewater characterisation

Table 5-1 shows the pesticide production wastewater characterisation of the different batches of wastewater collected at different times, hence the variation. The COD and BOD for the GAC-biological wastewater were 33750 ± 12996 mg/L and 11590 ± 6900 mg/L, respectively and the COD and BOD for the pilot plant wastewater were 49075 ± 212 mg/L and 6900 ± 35 mg/L, respectively indicating a high strength wastewater. These values were high when compared to other real pesticide production wastewater with COD values reported between 2500-5000 mg/L (Jin et al. 2010). The pesticide production wastewater investigated is known to contain lactic acid, glycolic acid, 2-ethylhexanol, n-butanol, i-butanol, isopropyl acetate. These pollutants are likely to be responsible for providing the high BOD and COD in the wastewater. The COD/BOD ratio of the wastewater was 7.11 indicating a poor biodegradable wastewater (Vollertsen and Hvitved-Jacobsen, 2002) (Table 5-1). Furthermore the carbon:nitrogen:phosphate ratio (22930:15:1 and 10118:0:1) indicated additional nutrients and alkalinity maybe required to sustain healthy microbial activity of the biological treatment as the ratio significantly differs from the recommended C:N:P ratio of 100:5:1 (Water Environment Federation, 2008). Other important parameters that are of major relevance when recommending treatment processes are the total suspended solids (TSS) and volatile suspended solids (VSS). Based on the high concentrations of TSS measured at 1437 ± 651 mg/L and 1539 ± 72 mg/L, The ratio between TSS and VSS indicated (10:1) that the solids are mostly inorganic, also emphasizing the need for a solids separation stage. Gupta et al. (2012) studied the removal of suspended solids of wastewater containing varies toxic compounds including pesticides. The results showed that removal up to 75% could be achieved when using a filtration, separation, sedimentation, and coagulation and floatation process as a primary treatment.

The pesticides present in the wastewater showed a wide range of concentrations from 0.12 (2,4-DP) – 59 mg/L (2,4-DCP) for the GAC-biological trials and 0.23 (2,4-DP) – 159 mg/L (2,4-DCP) for the pilot plant trials (Table 5-1). This is aligned with other studies reporting concentrations in real pesticide wastewater from <0.36 µg/L up to 2500 mg/L (Mcallister *et al.*, 1993; Soares, 2015).

Table 5-1. Pesticide production wastewater characterisation.

	Average and standard deviation
BOD (mg/ L)	6900 ± 35
COD (mg/ L)	49075 ± 212
COD/BOD*	7.11
pH	6.5
Alkalinity (mg CaCO3/L)	1555 ± 9
Total suspended solids (mg/ L)	1539 ± 72
Volatile suspended solids (mg/ L)	132 ± 93
Ammonium (mg/ L)	0.45 ± 0.07
Phosphate (mg/ L)	4.85 ± 0.07
C:N:P Ratio**	10118:0:1
Pesticides	
2,4-D (mg/ L)	32.59
2,4-DB (mg/L)	5.74
2,4-DP (mg/ L)	0.23
2,4-DCP (mg/L)	159.26
2,4,6-TCP (mg/L)	0.42
MCPA (mg/L)	49.03
MCPB (mg/L)	0.35

MCPP (mg/L)	45.91
PCOC (mg/L)	46.64

*COD/BOD of 3 indicates poor biodegradability (Vollertsen and Hvitved-Jacobsen, 2002);

** Ideal C:N:P ratio is 100:5:1 (Water Environment Federation, 2008).

5.4.2 Hybrid system: GAC + Biological Treatment

Continuous flow lab-scale columns were set-up to investigate the adsorption of pollutants to GAC as a pre-treatment at an EBCT of 10 min (Figure 5-3). In wastewater used in this experiment had a COD of 60150 ± 990 mg/L and pesticide concentrations of 174 mg/L phenoxy acids; 210 mg/L dichloro acids and 2 mg/L of 2,4,6-TCP. At 10 minutes EBCT the first pesticide to breakthrough was MCPB at 1020 BV followed by MCPA and MCPP at 1128 BV. Breakthrough was defined as the number of bed volumes (BV) when the concentration of the pesticide was the same in the effluent as in the influent.

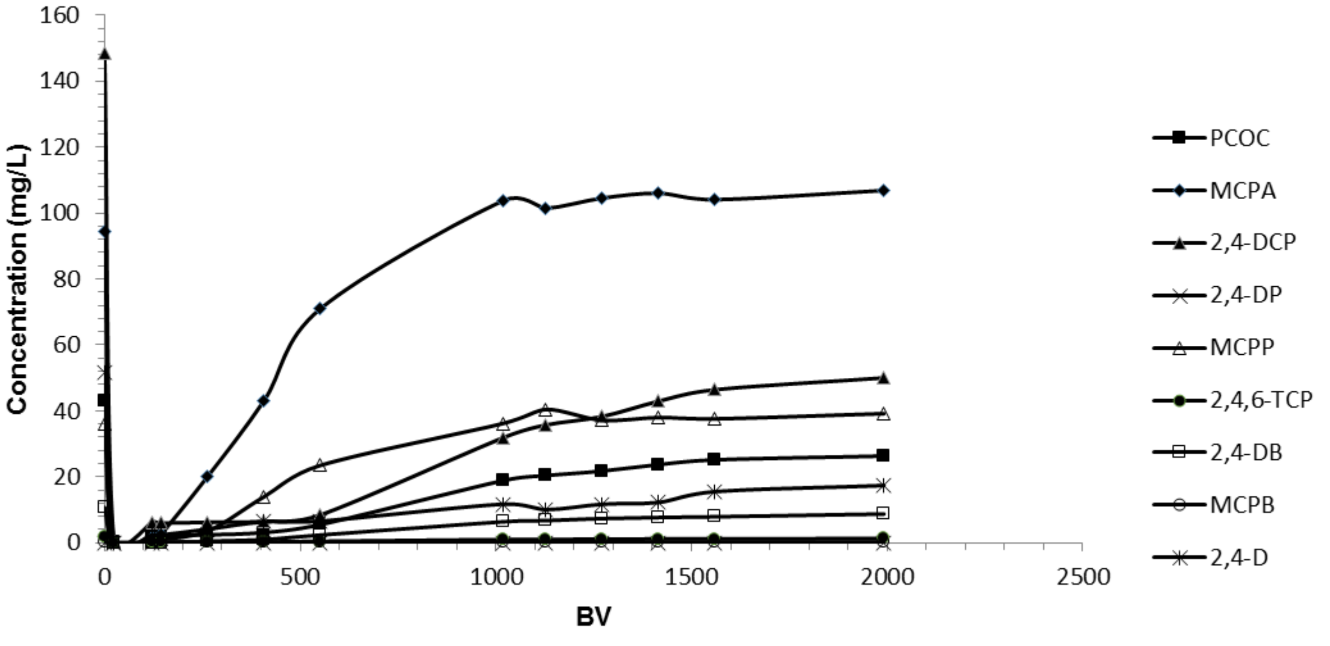


Figure 5-3. Breakthrough curves with 10 minutes EBCT in column experiments using GAC F-400 continuously fed with pesticide production wastewater.

After 408 BV GAC treatment the pesticide concentrations for phenoxy acids, dichloro acids and 2,4,6-TCP decreased to 60.4 mg/L (phenoxy acids), 13.8 mg/L (dichloro acids) and 0.3 mg/L (2,4,6-TCP), respectively showing removal rates of 65, 93 and 85%, respectively. After 552 BV GAC treatment the pesticide concentrations for phenoxy acids, dichloro acids and 2,4,6-TCP showed a decrease to 100, 17.4 and 0.4 mg/L, respectively showing removal rates of 43, 92 and 80%, respectively (Figure 5-5). The COD after GAC treatment at 552 BV was 17210 ± 71 mg/L, achieving a removal of 71%. The GAC pre-treatment was more effective adsorbing dichloro acids with removals >90%.

The pesticide wastewater was collected after treatment in the GAC columns at 120, 264, 408 and 552 BVs and its toxicity assessed using a respirometer. Respirometry is standard technique that measures the oxygen uptake rate (OUR) of an aerobic microbial population under controlled conditions and has been utilised in many studies to evaluate toxicity and biodegradability of various industrial wastewaters containing recalcitrant pollutants such as pesticides and pharmaceuticals (Meriç *et al.*, 2003; Kungolos, 2005; Farré *et al.*, 2007; Ballesteros Martín *et al.*, 2010). An OUR of 1.46 mg O_2/h.L was measured for the GAC pre-treated pesticide wastewater after 552 BV (at 100% concentration) (Figure 5-4). This was significantly lower when compared with the OUR in the control sample (deionised water and AS) at 19.69 mg O_2/h.L, indicating that the wastewater was toxic to the activated sludge organisms. The concentrations of pesticides were 2,4-D: 6.57 mg/L; 2,4-DB: 2.36 mg/L; 2,4-DP: 0.3 mg/L;2,4-DCP: 8.48 mg/L; MCPA: 71.06 mg/L; MCPB: 0.21 mg/L: MCPP: 23.49 mg/L; PCOC: 5.54 mg/L and 2,4,6-TCP: 0.43 mg/L. There is limited information about toxicity values for mixtures of pesticides to activated sludge, so it is difficult to indicate what compound(s) might be linked to the toxicity observed. Nevertheless the EC50 values to *Daphnia* and other aquatic invertebrates have been reported at 1 and 2.7-3.9 mg/L for PCOC and 2,4-DCP, so toxicity could be possibly due to these compounds (ECB, 2002; Fluka, 2009). It is necessary to consider the fact that different dilutions of the pesticide production wastewater would lead to different initial COD concentrations and therefore without inhibition would give different OURs. For instance, higher concentrations of pesticide wastewater would lead to higher OURs, due to higher concentrations of COD. Suggesting that the microorganisms are partially inhibited by more concentrated pesticide production wastewater as higher COD concentrations should lead to higher OURs therefore normalisation of the data to the initial COD should be considered.

When the GAC pre-treated pesticide wastewater was diluted by 50% and 75%, the OUR were 19.94 and 17.09 mg O_2/h.L, respectively, indicating no toxicity towards the activated sludge microorganisms (Figure 5-4). The toxicity of the wastewater was also measured before the GAC treatment and it was found that a 25% dilution would be required to prevent toxic effects to the activated sludge organisms. Hence, the GAC pre-treatment was effective at reducing toxicity to the biological process (Little *et al.*, 1980; Cheng *et al.*, 2007).

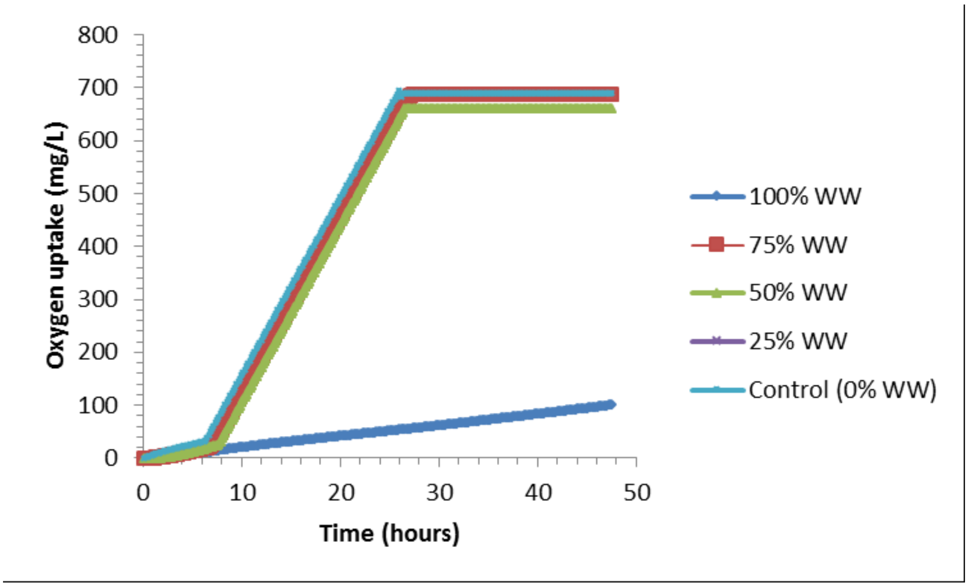


Figure 5-4. Oxygen uptake (mg/L) measured by the respirometer for different dilutions of the GAC pre-treated pesticide production wastewater after 552 BV GAC at 10 minutes EBCT. All tests were carried out in duplicate.

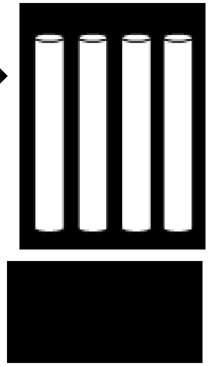
Batch tests with activate sludge biomass concentration of 7000 mg/L MLSS, mimicking a long SRT ASP, were also completed to investigate the removal pesticides in a biological aerated process, after the GAC pre-treatment and dilution to 75%. Initial concentrations of pesticides feed to the biological process were phenoxy acids (MCPA, MCPB, MCPP and PCOC), dichloro acids (2,4-D, 2,4-DP, 2,4-DB and 2,4-DCP) and 2,4,6-TCP were 45.3, 10.4 and 0.15 mg/L, respectively for

GAC pre-treated wastewater at 408 BV and 75, 13.1 and 0.3 mg/L, respectively for GAC pre-treated wastewater at 552 BV (Figure 5-5).

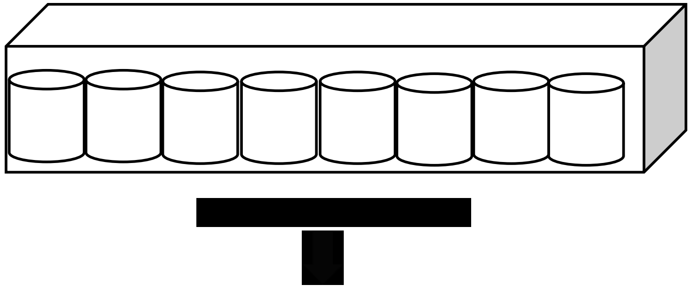
After biological treatment for a period of 48 hours, the pesticides concentration were reduced to 3.8, 0.9 and 0.3 mg/L for phenoxy acids, dichloro acids and 2,4,6-TCP, respectively (corresponding to removals of 94, 93 and 0%) when treating the GAC effluent obtained after 408 BV. The pesticides concentration were reduced to 24.6, 3.4 and 0.4 mg/L for phenoxy acids, dichloro acids and 2,4,6-TCP, respectively, (corresponding to removals of 75, 80 and 0%) when treating the GAC effluent obtained after 552 BV (Figure 5-5).

	Initial Conc (mg/L)
Phenoxy acids	174
Dichloro acids	210
2,4,6-TCP	2

➡



➡	408 BV		552 BV	
	Conc (mg/L)	% Removal	Conc (mg/L)	% Removal
Phenoxy acids	60.4	65	100	43
Dichloro acids	13.8	93	17.4	92
2,4,6-TCP	0.3	85	0.4	80



	408 BV			552 BV		
	Conc (mg/L)	% Removal	Total % Removal	Conc (mg/L)	% Removal	Total % Removal
Phenoxy acids	3.8	94	98	24.6	75	86
Dichloro acids	0.9	93	99.6	3.4	80	98
2,4,6-TCP	0.3	0	85	0.4	0	80

Figure 5-5. Concentrations (mg/L) and percentage removal of pesticide production wastewater at initial, after GAC and after biological treatment processes.

In order to evaluate the potential of the hybrid system composed of GAC as pre-treatment followed by a biological process to treat the high strength pesticide wastewater, the system must be appraised as a whole. The overall pesticides removals were 98.0% (phenoxy acids), 99.6% (dichloro acids) and 85.0% (2,4,6-TCP) for 408 BV GAC. If the GAC columns were run until 552 BV, the overall pesticides removals were 86% (phenoxy acids), 98% (dichloro acids) and 80% (2,4,6-TCP) (Figure 5-5). The effluent concentrations for pesticides with defined EQS were: 2,4-D: 1.7 mg/L; 2,4-DCP: 1.3 mg/L; MCPP: 5.2 mg/L and MCPA: 17.7 mg/L (for 552 BV GAC) , respectively. The EQS for these compounds are 0.3 µg/L (2,4-D), 20 µg/L (2,4-DCP), 18 µg/L (MCPP) and 2 µg/L (MCPA). At these concentrations the EQS discharge limits would have been breached.

This study clearly demonstrated that using GAC as pre-treatment has many advantages such as low contact time; high pesticide removal efficiencies (>75%); decreased toxicity to the following biological process, reducing the need for wastewater dilution and respective footprint of the biological process. Nevertheless the GAC columns became rapidly saturated with pesticides reaching breakthrough after only 1020 BV (Figure 5.3). This entails that the GAC would require frequent regeneration, which is costly, between £0.84-1.32/kg. Regeneration frequencies should be between 4-12 months, for the process to be economically viable (EPA, 2002). To decrease the frequency of regeneration, longer EBCT might be applied, but this obliges to increase in the number of GAC columns on site, to treat the same flow, increasing capital costs. Hence, it is important to reach a good balance between EBCT and the number of GAC columns on site (capital cost) and regeneration frequency (operational cost) to ensure economic efficiency. When treating industrial wastewater with GAC, EBCT have been reported to vary between 30-540 minutes (Hung *et al.*, 2005), hence this study operated at relatively low EBCT. Furthermore the pesticide production wastewater contained a high concentration of COD (33750 ± 12996 mg/L) and TSS (1437 ± 651 mg/L) that have been shown to reduce the life-time and effectiveness of GAC (Çeçen and Aktaş, 2011). For the GAC process to work effectively, low TSS (<20 mg/L) and low COD and BOD are recommended (EPA, 2002). Previous experiments as demonstrated in chapter 4 have shown that GAC is significantly reduced by the matrix of the wastewater when comparing synthetic solutions and real pesticide wastewater for instance GAC capacity for 2,4-DCP in synthetic solution was 427.3 mg/g and in real wastewater 39.2 mg/g showing that the wastewater has other compounds that compete for the adsorption sites in the GAC. Although the hybrid system composed of GAC as pre-treatment followed by a biological process, presented many advantages and high efficiency, this process is not likely to be economically feasible due high organic matter in the wastewater with the GAC columns becoming rapidly saturated requiring frequent GAC regeneration.

5.4.3 Hybrid treatment process with MBR

The pesticide production wastewater was treated using various hybrid systems: Hybrid System 1 (MBR+GAC), Hybrid System 2 (MBR+GAC+UV) and Hybrid System 3 (MBR+UV). The initial concentrations of the pesticides remained stable throughout the pilot trials with average influent concentrations of 167.96 ± 1.07 mg/L, 241.09 ± 2.07 mg/L and 5.05 ± 0.50 mg/L mg/L for phenoxy acids, dichloro acids and 2,4,6-TCP, respectively and COD and BOD concentrations 45970 ± 1032 mg/L and 8290 ± 611 mg/L. The operational period was divided in two: days 0-26 without addition of nutrients and alkalinity and day 26-35 with addition of nutrients and alkalinity. After dilution of the wastewater to 25%, the MBR reached stable effluent concentrations within 5 days of operation, demonstrating that a short start-up period was required (Figure 5-6). This is different from other studies that suggest up to 6 months acclimation periods for 2,4-DCP in activated sludge (Quan, et al., 2004). The fact that no biomass was wasted in the MBR has been shown to improve microbial degradation of the pollutants (Spring et al, 2007). The average of phenoxy acids, dichloro acids and 2,4,6-TCP concentrations in the MBR effluent were 17.20 ± 2.90, 18.41 ± 0.13, and 0.93 mg/L, respectively, giving average removal efficiencies of 57%, 66% and 27%, respectively (Figure 5.6). The total pesticide (phenoxy acids, dichloro acids and 2,4,6-TCP) removal efficiency was 58% (Figure 5-6). The removals of COD and BOD reached 71 and 50%, respectively (Figure 5-7).

When nutrients and alkalinity were added to the MBR, the average of phenoxy acids, dichloro acids and 2,4,6-TCP concentrations in effluent were 9.49 ± 1.90, 10.31 ±

0.14, and 0.21 mg/L, respectively, giving average removal efficiencies of 97%, 94% and 83%, respectively (Figure 5.6). The total pesticide (phenoxy acids, dichloro acids and 2,4,6-TCP) removal efficiency was 94% (Figure 5-6). The removals of COD and BOD reached 88 and 72%, respectively (Figure 5-7).

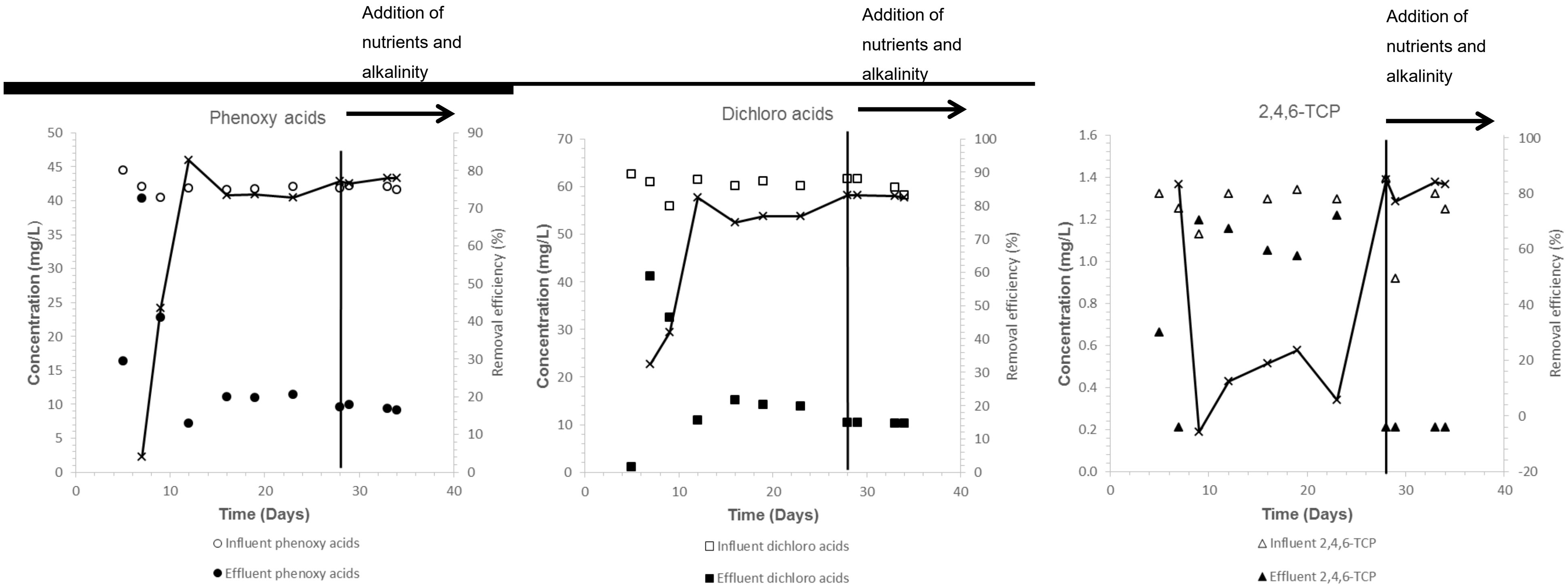


Figure 5-6. Influent and effluent concentrations (mg/L) and percentage removal of pesticide in the MBR pilot-plant without additional nutrients and alkalinity (days 0-26) and with additional nutrients and alkalinity (days 26-35).

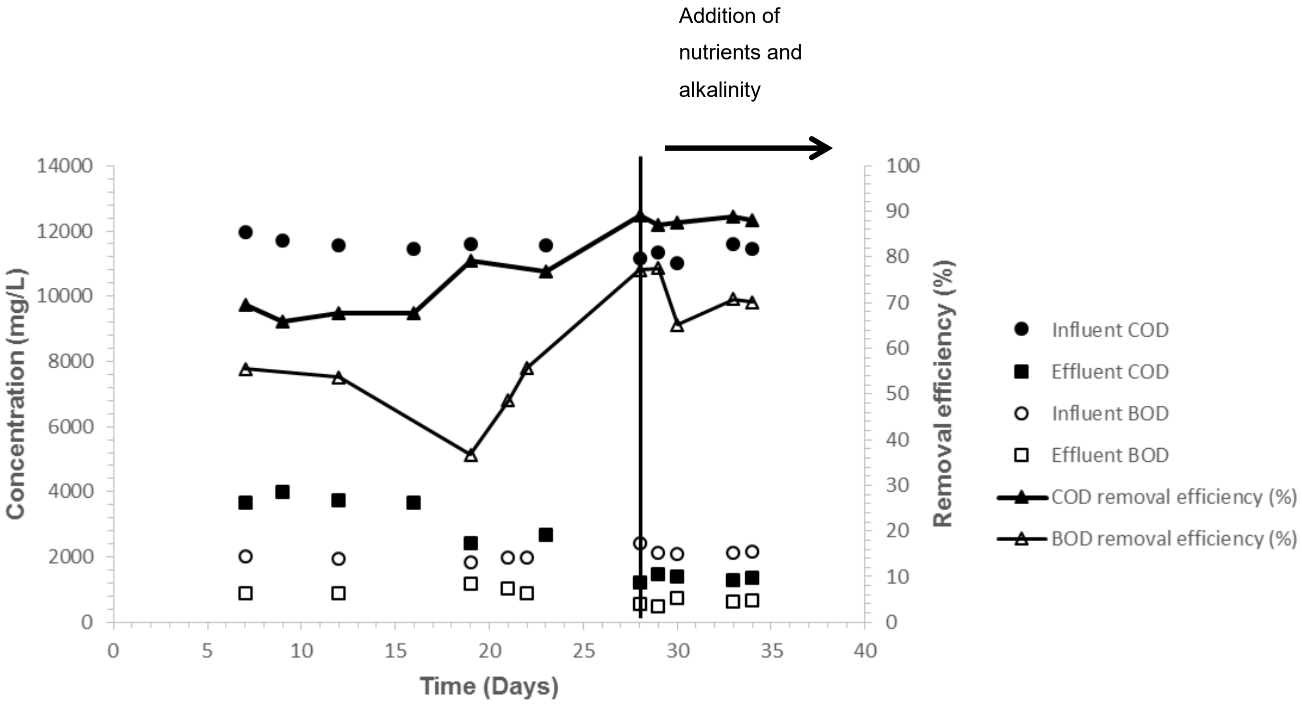


Figure 5-7. Influent and effluent BOD and COD concentrations (mg/L) and percentage removal in the MBR pilot-plant without additional nutrients and alkalinity (days 0-26) and with additional nutrients and alkalinity (days 26-35).

The pesticide production wastewater is nutrient deficient with low ammonium (0.45 mg/L) and phosphate (4.85 mg/L) concentrations contrasting with a very high concentration of COD at 49075 mg/L (Table 5-1). Ammonia and phosphate are essential nutrients for all living organisms and are used in used in the microbial cells to maintain biochemical activity (Tchobanoglous *et al.*, 2003). The wastewater had a carbon:nitrogen:phosphate ratio of 10118:0:1 which indicates that additional nutrients maybe required to increase the efficiency of the biological treatment as the ratio significantly differs from the recommended C:N:P ratio of 100:5:1 (Water Environment Federation, 2008). It can be seen that adding nutrients and alkalinity increased pesticide as well as carbon removal, acting as a microbial stimulant which enhanced the efficiency of the biological treatment as previously discussed (Burgess et al. 1999; Water Environment Federation, 2008). The MLSS in the MBR at the start and end of the operation period were 7622 and 9910 mg/L, also indicating the microorganisms were well established.

The MBR was ran at constant flux of 8 LMH and the membrane permeability was accessed throughout the operational period by measuring trans-membrane pressure (Figure 5.8). Trans-membrane pressure (TMP) is the pressure difference between the filtrate side and the permeate side of the membrane. When TMP increases it indicates membrane fouling as the pores on the membrane are starting to become blocked. The TMP remained <60 mbar for 400h (16.6 days) indicating low membrane fouling. After 400h the TMP started to increase to 110 mbar and at 440h the blocked membrane channel was closed and another was open. This resulted in the TMP pressure decreasing to <50 mbar and remained stable for over 140 h (5.8 days). Between 580-695h the TMP increased to 162 mbar, once again indicating membrane fouling. When this happens the membrane fouling can be controlled by hydraulic, chemical or physical cleaning (Judd and Judd, 2006; Çeçen and Aktaş, 2011). In this study the membrane was removed from the reactor, cleaned with a water hose (physically cleaning) and used again. After cleaning the TMP was restored to the original levels of <50 mbar, and remained low from 695-840h (Figure 5-8). This showed that the fouling of the membrane was reversible, suggesting that physical cleaning (or increased air sparging) would enough to clean the membrane and reduce the amount of membrane non-running time in weekly or by-weekly operation routine (Iorhemen et al., 2017 Kitagawa et al., 2012). On the other side, the MBR was ran at rather conservative flux of 8 LMH. Industrial wastewater treatment MBRs can operate up to 25- 35 LMH (Judd and Judd, 2006). As the TMP pressure in this study remained low and fouling could be easily controlled, higher fluxes should be investigated with the benefit of reducing membrane area in the reactor.

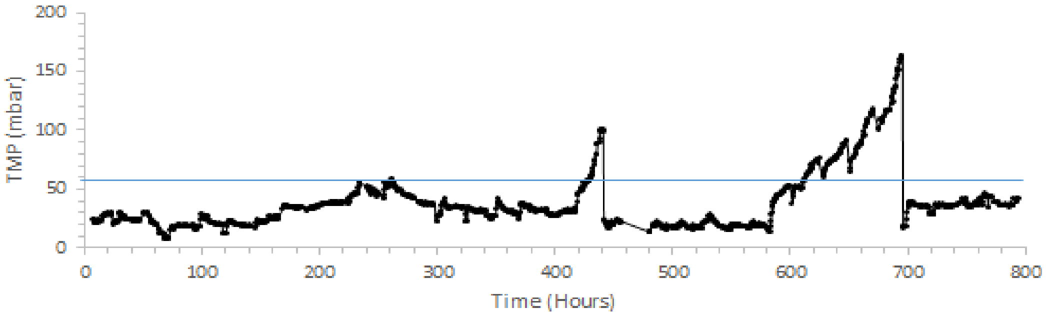


Figure 5-8. Trans-membrane pressure of the MBR during the operational period of 34 days.

5.4.4 Hybrid System 1: MBR – GAC

The effluent from the MBR was then treated in GAC columns at 30 and 60 minutes EBCTs. The breakthrough curves show a typical shape with concentrations of pesticides increasing with number of bed volumes (Figure 5-9). At an EBCT of 30 min, after 1040 BV the concentration of 2,4-DB, 2,4-DCP, and 2,4,6-TCP were below 1 mg/L but for other pesticides the concentrations were higher (2,4-DCP: 4.23 mg/L; MCPA: 5.03 mg/L; MCPP: 5.36 mg/L and PCOC: 2.01 mg/L). As expected, increasing the EBCT to 60 min resulted in an increase in pesticide removal. At an EBCT of 60 min, after 1040 BV the concentration of 2,4-DB, 2,4-DCP, and 2,4,6-TCP were below 0.06 mg/L but for other pesticides the concentrations were higher (2,4-DCP: 0.56 mg/L; MCPA: 1.23 mg/L; MCPP: 0.48 mg/L and PCOC: 0.50 mg/L). In both GAC columns the compound that showed the lowest adsorption to GAC was MCPA. Studies have been reported that GAC media has been able to keep adsorbing up to 20 months before regeneration was required, with initial concentrations around 3.7-4.1 µg/L and EBCTs of 10.3 and 14 minutes (Knappe *et al.*, 1997). However, these concentrations are much lower than the pre-treated MBR wastewater, and therefore it is anticipated that the GAC in this study would require regeneration more frequently.

Addition of
nutrients and
alkalinity

Addition of
nutrients and
alkalinity

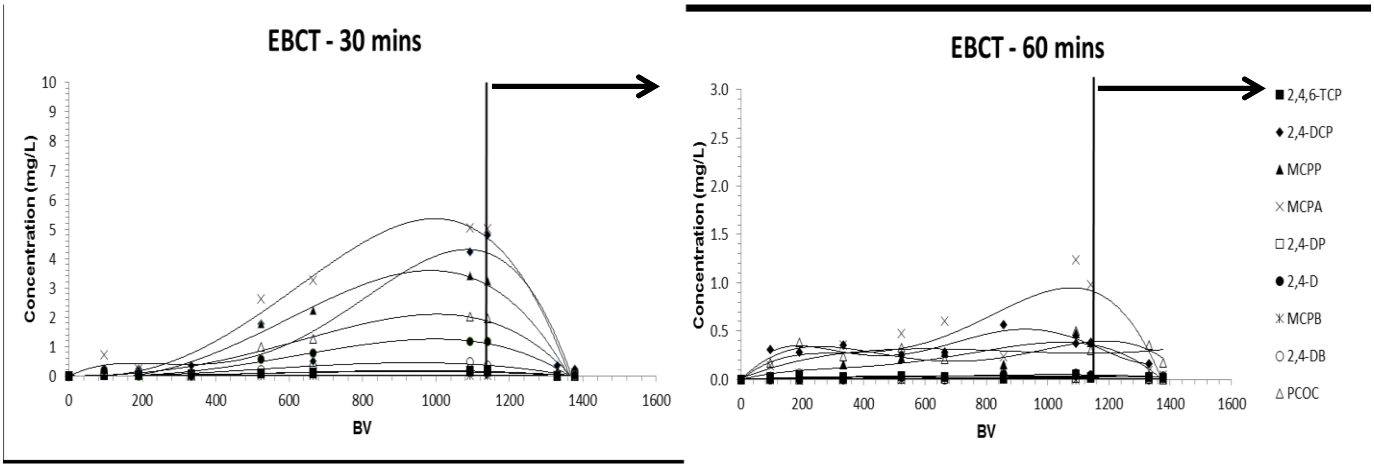
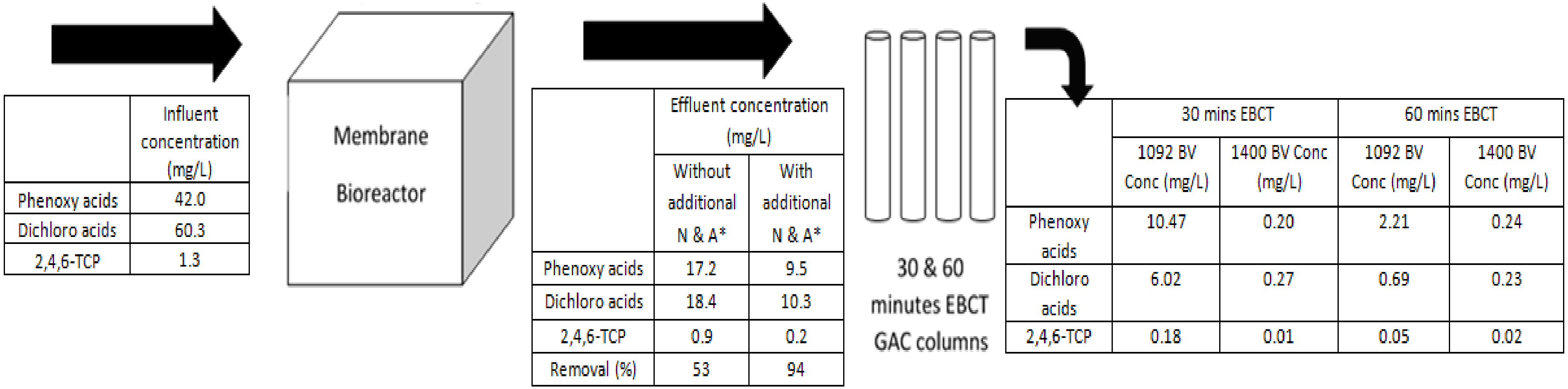


Figure 5-9. Breakthrough curves with 30 and 60 minutes EBCT in column experiments using GAC F-400 continuously fed with MBR effluent.

After 1140 BVs, the GAC columns were fed with MBR effluent when additional nutrients and alkalinity were dosed to the MBR (Figure 5-9). At 30 min EBCT, the pesticide concentrations for phenoxy acids, dichloro acids and 2,4,6-TCP decreased to 0.20, 0.28 and 0.01 mg/L. At 60 min EBCT, the pesticide concentrations for phenoxy acids, dichloro acids and 2,4,6-TCP were 0.24, 0.23 and 0.012 mg/L. The results show a significant reduction in pesticide concentration in both 30 and 60 minutes EBCTs suggesting increased adsorption capacity of the GAC for this type of MBR effluent. It is not clear why the GAC adsorption capacity increased but some factors that might be at play include lower COD and pesticide concentrations in the influent of the GAC columns. The COD concentration was reduced by 2.5 fold, after the MBR was dosed with alkalinity and nutrients (from 3361 mg/L to 1346 mg/L) and the total pesticide concentration was reduce by 1.8 fold (from 36.54 mg/L to 20.01 mg/L). The kinetics of GAC adsorption is strongly influenced by the concentration of the sorbate and competing organic compounds and hence a reduction in their concentration yields higher adsorption capacities (Cooney, 1998). Furthermore, the fact that the GAC showed increased capacity after being fed with a lower strength wastewater seems to indicate a displacement of a “physical coating”, once again indicating that organic compounds (COD) strongly impacted the GAC efficiency.

Total removal (phenoxy acids, dichloro acids and 2,4,6-TCP) for pesticide wastewater treated without nutrients and alkalinity (1092 BV) and with nutrients and alkalinity (1400 BV) GAC for 60 minutes EBCT were 97% and 99.5%, respectively.

For the individual pesticide concentrations at 1400 BV (60 minutes EBCT) with set discharge limits (2,4-D, 2,4-DCP and MCPP) the results were; 2,4-D 0.029 mg/L, 2,4-DCP 0.166 mg/L, MCPP 0.019 mg/L and MCPA 0.048 mg/L. At these concentrations the EQS discharge limits would have been breached with limits set at 0.3 µg/L (2,4-D), 20 µg/L (2,4-DCP), 18 µg/L (MCPP) and 2 µg/L (MCPA).



	Influent concentration (mg/L)
Phenoxy acids	42.0
Dichloro acids	60.3
2,4,6-TCP	1.3

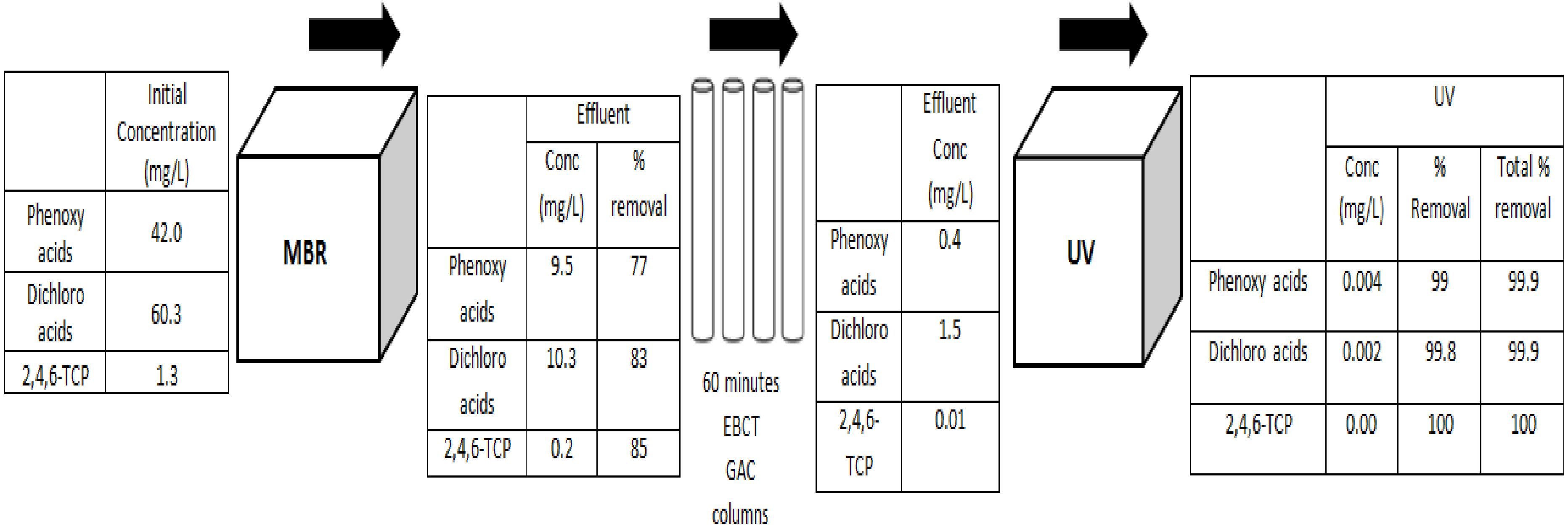
	Effluent concentration (mg/L)	
	Without additional N & A*	With additional N & A*
Phenoxy acids	17.2	9.5
Dichloro acids	18.4	10.3
2,4,6-TCP	0.9	0.2
Removal (%)	53	94

	30 mins EBCT		60 mins EBCT	
	1092 BV Conc (mg/L)	1400 BV Conc (mg/L)	1092 BV Conc (mg/L)	1400 BV Conc (mg/L)
Phenoxy acids	10.47	0.20	2.21	0.24
Dichloro acids	6.02	0.27	0.69	0.23
2,4,6-TCP	0.18	0.01	0.05	0.02

Figure 5-10. Concentrations (mg/L) and percentage removal of pesticide production wastewater at initial, after MBR and after GAC treatment processes. *N & A – Nutrients and alkalinity

5.4.5 Hybrid treatment process with MBR – GAC –UV

Combining MBR, GAC and UV to treat the pesticide production wastewater showed total removal levels for phenoxy acids, dichloro acids and 2,4,6-TCP were 99.9, 99.9 and 100%, respectively with all pesticide concentration levels below 0.004 mg/L (Figure 5-11). When comparing MBR-GAC-UV (Figure 5-11) and MBR -UV (Figure 5-12) it can be seen that phenoxy acids concentrations were 50% lower, where dichloro acids and 2,4,6-TCP have negligible difference. However all final values in Figure 5-12 are below the LOD therefore could be at much lower values. This hybrid system complies with the EQS discharge limits of 0.3 µg/L (2,4-D), 20 µg/L (2,4-DCP), 18 µg/L (MCPP) and 2 µg/L (MCPA).



	Initial Concentration (mg/L)
Phenoxy acids	42.0
Dichloro acids	60.3
2,4,6-TCP	1.3

	Effluent	
	Conc (mg/L)	% removal
Phenoxy acids	9.5	77
Dichloro acids	10.3	83
2,4,6-TCP	0.2	85

	Effluent Conc (mg/L)
Phenoxy acids	0.4
Dichloro acids	1.5
2,4,6-TCP	0.01

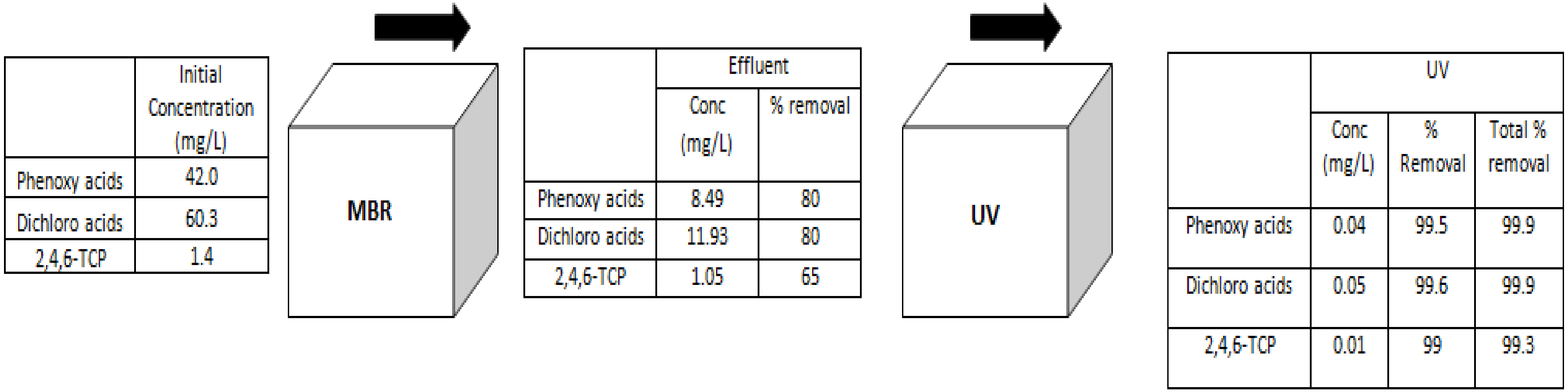
	UV		
	Conc (mg/L)	% Removal	Total % removal
Phenoxy acids	0.004	99	99.9
Dichloro acids	0.002	99.8	99.9
2,4,6-TCP	0.00	100	100

Figure 5-11. Concentrations (mg/L) and percentage removal of pesticide production wastewater at initial, after MBR and after UV treatment processes.

5.4.6 Hybrid treatment process with MBR – UV

Combining MBR with UV showed total removal efficiencies for phenoxy acids, dichloro acids and 2,4,6-TCP were 99.9, 99.9 and 99.3%, respectively with all pesticide concentration levels below 0.05 mg/L (Figure 5-12). For the individual pesticide concentrations with set discharge limits (2,4-D, 2,4-DCP and MCPP) the results were; 2,4-D 0.04 mg/L, 2,4-DCP 0.005 mg/L, MCPP 0.01 mg/L and MCPA 0.005 mg/L. At these concentrations the EQS discharge limits 2,4-D would have been breached with limits set at 0.3 µg/L (2,4-D).

This was due to the compounds been able to absorb UV light and photolyse at 254 nm. The use of UV photolysis process has been reported to remove low concentrations of pesticides (De la Cruz *et al.*, 2012). De la Cruz *et al.*, (2012) studied the degradation of contaminants including pesticide MCPP by UV in wastewater effluent that had been previously treated by AS. The results showed after 10 minutes of UV radiation at 254 nm MCPP was removed by 84%, with initial concentration been 34 ng/L this concentration was very low compared to the pesticide wastewater investigated in this study. A number of other studies have also presented pollutants been degraded by direct UV photolysis (Sanches et al., 2010). The process involves excitation of the organic compounds which encourages the transfer of an excited electron to form an organic radical that can then react with oxygen. Using a lower wavelength of 254 nm is required to form hydroxyl radicals (Gonzalez *et al.*, 2004), however UV photolysis in is dependent on the pollutants been targeted (Kim, et al., 2009).



	Initial Concentration (mg/L)
Phenoxy acids	42.0
Dichloro acids	60.3
2,4,6-TCP	1.4

	Effluent	
	Conc (mg/L)	% removal
Phenoxy acids	8.49	80
Dichloro acids	11.93	80
2,4,6-TCP	1.05	65

	UV		
	Conc (mg/L)	% Removal	Total % removal
Phenoxy acids	0.04	99.5	99.9
Dichloro acids	0.05	99.6	99.9
2,4,6-TCP	0.01	99	99.3

Figure 5-12. Concentrations (mg/L) and percentage removal of pesticide production wastewater at initial, after MBR and after UV treatment processes.

Table 5-2 compares the hybrid processes tested for treating pesticide wastewater. It can be seen from the results that the recommendation to treat the wastewater would be either MBR-GAC-UV or MBR-UV with total pesticide removals of 99.9 and 99.6%, respectively. However 2,4-D breaches the limit of 0.3 µg/L. Utilising the MBR-UV hybrid system would reduce operational and set up costs as columns and GAC would don’t be required.

The GAC-MBR system is not an effective system as this system would breach the EQS limits. Combining MBR and GAC to create these hybrid systems produced an enhanced high quality effluent, as the no suspended solid effluent with a lower concentration of organic matter from the MBR allowed the GAC to target and remove the remaining recalcitrant pollutants (Melin *et al.*, 2006).

Table 5-2. Comparing hybrid treatment processes for pesticide production wastewater.

Hybrid system with nutrients and alkalinity dose to the MBR												
Hybrid System 1 (MBR+GAC)	COD (mg/L)	BOD (mg/L)	Dichloro acids (µg/L)				Phenoxy acids (µg/L)				
			2,4-D	2,4-DB	2,4-DP	2,4-DCP	MCPA	MCPB	MCPP	PCOC	2,4,6-TCP (µg/)
Influent	45970	8290	29079.00	7962.83	225.00	203824.58	78812.25	280.00	43685.17	45184.25	5052.25
After dilution	11493	2073	7269.75	1990.71	225.00	50956.15	19703.06	70.00	10921.29	11296.06	1263.06
MBR effluent	1346	605	667.25	579.79	90.00	8968.50	4679.50	30.18	2747.00	2035.25	213.33
GAC (60 min EBCT effluent)	1422	115	34.55	21.30	9.30	308.17	372.43	9.57	147.18	277.62	22.57
Total system removal (%)	97	99	99.88	99.73	95.87	99.85	99.53	96.58	99.66	99.39	99.55
Average removal for all pesticides (%)			98.89								
Average removal per pesticide group (%)			98.83				98.79				99.55
Removals after dilution (%)	88	94	99.52	98.93	95.87	99.40	98.11	86.33	98.65	97.54	98.21
Average removal for all pesticides (%)			96.95								
Average removal per pesticide group (%)			98.43				95.16				98.21
Hybrid System 2 (MBR+GAC+UV)	COD (mg/L)	BOD (mg/L)	Dichloro acids (µg/L)				Phenoxy acids (µg/L)				
			2,4-D	2,4-DB	2,4-DP	2,4-DCP	MCPA	MCPB	MCPP	PCOC	2,4,6-TCP (µg/)
Influent	45970	8290	29079.00	7962.83	225.00	203824.58	78812.25	280.00	43685.17	45184.25	5052.25
After dilution	11493	2073	7269.75	1990.71	225.00	50956.15	19703.06	70.00	10921.29	11296.06	1263.06
MBR effluent	1346	605	667.25	579.79	90.00	8968.50	4679.50	30.18	2747.00	2035.25	213.33
GAC (60 min EBCT effluent)	1422	115	34.55	21.30	9.30	308.17	372.43	9.57	147.18	277.62	22.57
UV effluent			0.37	0.37	0.37	0.65	0.01	0.50	0.01	3.91	0.02
Total system removal (%)	97	99	100.00	100.00	99.83	100.00	100.00	99.82	100.00	99.99	100.00
Average removal for all pesticides (%)			99.96								
Average removal per pesticide group (%)			99.96				99.95				100.00
Removals after dilution (%)	88	94	99.99	99.98	99.83	100.00	100.00	99.29	100.00	99.97	100.00
Average removal for all pesticides (%)			99.90								
Average removal per pesticide group (%)			99.95				99.81				100.00
Hybrid System 3 (MBR+UV)	COD (mg/L)	BOD (mg/L)	Dichloro acids (µg/L)				Phenoxy acids (µg/L)				
			2,4-D	2,4-DB	2,4-DP	2,4-DCP	MCPA	MCPB	MCPP	PCOC	2,4,6-TCP (µg/)
Influent	45970	8290	29079.00	7962.83	225.00	203824.58	78812.25	280.00	43685.17	45184.25	5052.25
After dilution	11493	2073	7269.75	1990.71	225.00	50956.15	19703.06	70.00	10921.29	11296.06	1263.06
MBR effluent	1346	605	667.25	579.79	90.00	8968.50	4679.50	30.18	2747.00	2035.25	213.33
UV effluent			39.60	0.37	0.75	5.00	5.00	1.00	7.07	22.63	5.00
Total system removal (%)	97	93	99.86	100.00	99.67	100.00	99.99	99.64	99.98	99.95	99.90
Average removal for all pesticides (%)			99.89								
Average removal per pesticide group (%)			99.88				99.89				99.90
Removals after dilution (%)	88	71	99.46	99.98	99.67	99.99	99.97	98.57	99.94	99.80	99.60
Average removal for all pesticides (%)			99.66								
Average removal per pesticide group (%)			99.77				99.57				99.60

5.5 Conclusion

The GAC-biological hybrid system showed that after GAC treatment the pesticide production wastewater was not toxic to the aerobic microorganisms at 75% dilution, whereas prior to GAC treatment the pesticide wastewater was toxic to microorganisms above 25% dilution. However after 552 BV of GAC and biological treatment removals efficiencies were low with phenoxy acids, dichloro acids and 2,4,6-TCP been 86, 98 and 83%, respectively.

The MBR-GAC pilot scale was effective with total pesticide removals of 53% after dosing with addition nutrients and alkalinity to the MBR with total removal efficiencies increased to 94%. The addition of nutrients and alkalinity increased the use of recalcitrant pesticides as a food source when an adequate and balanced nutrient supply was provided. Furthermore there were increases in removal efficiencies for BOD from 50% to 72% and COD from 71% to 88%. However for the individual pesticide concentrations at 1400 BV (60 minutes EBCT) with set discharge limits (2,4-D, 2,4-DCP and MCPP) the results were; 2,4-D 0.029 mg/L, 2,4-DCP 0.166 mg/L, MCPP 0.019 mg/L and MCPA 0.048 mg/L showing that the EQS discharge limits would have been breached. It can also be seen that running at higher EBCTs increases the capacity of the GAC. Overall, the GAC experiments demonstrated this treatment option with at these initial concentrations was an efficient and reliable treatment option for treating this pesticide production wastewater.

The MBR-UV and MBR-GAC-UV hybrid systems, where extremely effective with total the pesticide concentrations of 0.01 mg/L and 0.006 mg/L, respectively and total pesticide removals of >99.3 and >99.9%, respectively. The MBR-GAC-UV complies with full EQS limits whereas MBR-UV system breaches the EQS limit for 2,4-D. However further tests could to completed to ensure the 2,4-D is reduced further. Using MBR-UV than MBR-GAC-UV would be a much cheaper alternative as there would not be the need for GAC columns and the expense of GAC regeneration.

5.6 References

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█ Discussion

Numerous investigations on pesticide removal have been carried out using biological (Mcallister *et al.*, 1993; Bernhard et al., 2006), physical (Knappe *et al.*, 1997; Gupta *et al.*, 2011), chemical (Barbusiński and Filipek, 2001; Kowalska *et al.*, 2004) and combined hybrid processes such as (Shawaqfeh, 2010; Moreira *et al.*, 2012; Vilar *et al.*, 2012). However research to date has focused on pesticide degradation in mixtures of one to four different pesticides, the more common ones; 2,4-D, 2,4-DCP, MCPA, AND PCOC (Irmak et al., 2004; Kowalska *et al.*, 2004; Quan *et al.*, 2004). No studies have been reported on experimenting with pesticide production wastewater similar to the one investigated in this thesis.

An understanding of the pesticides; 2,4-dichlorphenoxy acetic acid (2,4-D); 4-(2,4-dichlorphenox) propionic acid (2,4-DP); 4-(2,4-dichlorophenox) butyric acid (2,4-DB); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chlororthocresol (PCOC); 4-chloro-2-methyl phenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy) butyric acid (MCPB) and 2-(4-chloro-2-methylphenoxy) acetic acid (MCPP) physical and chemical characteristics and existing treatment processes that have been reported were evaluated in the literature review (Chapter 2) in order to determine suitable treatment options to treat the pesticide production wastewater.

The development of a fast high performance liquid chromatography (HPLC) method and sensitive gas chromatography mass spectrometry (GC-MS) method (Chapter 3) meant that samples could be analysed quickly and at very low concentrations (<0.01 mg/L). The HPLC method, unlike the GC-MS methods (Rompa et al., 2005; Bernhard et al., 2006; Gu *et al.*, 2010), did not require large amounts of solvents, extraction steps, etc. and it was very suitable to analyse the pesticides in the wastewater since they were found at high concentrations, in order of mg/L. Both methods were validated giving certainty that could produce accurate, reliable and reproducible results. For HPLC a gradient method required the use of the Fortis cyano column, changes in flow rates and mobile phase to be able to separate the nine target pesticides. For GC-MS, the initial method was based on Rompa et al. (2005), however the cartridges used during solid phase extraction (SPE) did not produce good recovery and some pesticides were not retained on the cartridges. Further development was required and the several different cartridges were tested. The cartridges that gave good recoveries and retained the pesticides were Sep-Pak Vac 6cc (500 mg) tC18 cartridges (Waters).

Characterisation of the pesticide production wastewater (Chapter 4 and Chapter 5) showed high chemical oxygen demand (COD) concentrations (33750-49075 mg/L). Further tests demonstrated that diluting the wastewater to 25% and adding aerobic microorganisms at a 7000 mg/L mixed liquor suspended solids (MLSS) removed 37, -64 and 30% for phenoxy acids, dichloro acids and 2,4,6-TCP, respectively. Accumulation of 2,4,-DB was observed during the tests. Adding additional nutrients (1.7 g/L NH_4 and 0.23 g/L PO_4) and alkalinity (0.1 g/L) (Chapter 4) were seen to enhance microbial activity increasing the pesticides removal efficiency (by 25%) and there was no accumulation in 2,4-DB. By adding the additional nutrients made the wastewater a more suitable food source for the aerobic microorganisms and provided the recommended carbon:nitrogen:phosphate (C:N:P) ratio of 100:5:1 (Water Environment Federation, 2008). It was also reported that nitrogen and phosphate can be growth limiting factors for the aerobic microorganisms if there are insufficient concentrations present. It was observed that acclimatising the activated sludge microorganisms for a period of 103 days produced inconclusive results due the variability of the wastewater fed to the biomass. Anaerobic treatability tests showed that anaerobic microorganisms were unable to cope with the pesticide production wastewater dilutions greater than 1% and therefore was deemed to be a non-economical viable treatment option and was not pursed any further.

Granular activated carbon (GAC) has been reported to successful be at removing the pesticides investigated in the project by various studies (Knappe *et al.*, 1997; Gupta *et al.*, 2011) and this also be seen in the physical and chemical properties of the pesticides with $\log_{kd}$ values above 1.5 (Table 2-2). During batch tests, GAC showed good adsorption of pesticides and most of the pesticides have equilibrium times within 5 hours and 58-100% pesticide removal was observed within 24 hours. Column tests carried out showed GAC regeneration was required between 599-1374 bed volumes (BV) when using 3-30 minutes empty bed contract time (EBCT). Using a higher EBCT would entail using a lower flow rate and as a result less wastewater would be treated at a time. Therefore increasing the number of columns used would be necessary but on the other side, regeneration would not be necessary as frequently, as for the lower EBCTs. Typical EBCTs for industrial wastewater treatment is in the range of 30-540 minutes (Hung et al., 2005). The low EBCTs tested in this study allowed a larger volume of wastewater to be treated at one time when compared to the typical EBCTs. It was deemed that using GAC as a treatment would be an efficient and reliable treatment option for treating this pesticide production wastewater.

When carrying out treatment using advanced oxidation processes (AOPS) (Fenton process and ultraviolet/hydrogen peroxide (UV/H_2O_2) on the pesticides present in the wastewater, literature suggested that high removal efficiencies between 89-100% could be obtained (Barbusiński et al., 2001; Kowalska *et al.*, 2004; James et al., 2014). However, experiments carried out showed that Fenton process showed negligible pesticide removal even when ten-fold of the stoichiometric concentration of H_2O_2 was added, in relation to the pesticides concentrations. Experiments completed using UV/H_2O_2 (Chapter 4) showed UV photolysis was a more efficient process to remove the pesticides without the presence of H_2O_2 due to the higher removal percentages. This was due to the compounds been able to absorb UV light and photolyse at 254 nm. The results suggested that H_2O_2 reduced pesticide removal by filtering the UV light. This was confirmed and further supported by a further increase of the H_2O_2 concentration to 6250 mg/L which resulted in a further reduction in pesticide removal levels. It was clear that the pesticides in this study were able to be degraded by UV photolysis alone at an intensity of 30 W/m^3, with total pesticide removal efficiencies of 50%. Both AOPs showed no enhancement in pesticide removal when adding H_2O_2. When compared to literature, the concentrations used in existing studies were in the range of µg/L for Fenton process (Barbusiński et al., 2001) and for UV/H_2O_2 (James et al., 2014). The wastewater investigated in this study had a significantly higher pesticide concentration (mg/L) and with a complex matrix (e.g. high alkalinity of 1069 mg/L which can act as a radical scavenger).

Evaluating the results from the individual biological, physical and chemical processes in chapter 4 (Task 2). The aim of this project was to combine a successful hybrid process that would be able to treat the pesticide production wastewater to a high quality effluent that would meet discharge limits. Chapter 5 (Task 3) combines the most effective removal processes to successful hybrid process. This involved a membrane bioreactor (MBR) coupled with activated sludge, GAC adsorption and UV photolysis processes. GAC was experimented as a pre-treatment and post-treatment to determine the most efficient way of treating the pesticide production wastewater. Ultraviolet photolysis experiments were completed as a post-treatment after MBR treatment and after MBR and GAC treatment. Respirometry experiments were completed on pesticide production wastewater that was treated with GAC to determine the toxicity of the wastewater towards microorganisms.

The GAC-biological hybrid system was effective at removing phenoxy acids and dichloro acids with removal efficiency observed at 67 and 74% at 552 BV GAC whilst removal efficiencies for 2,4,6-TCP was 0%. The biological process involved using a respirometer to determine the toxicity of the pre-treated wastewater. From previous experiments, the pesticides production wastewater was proven to be toxic to microorganisms above 25% wastewater dilutions (Chapter 4). Other existing literature using the respirometer have also shown pesticides to affect the growth of activated sludge microorganisms (Pai *et al.*, 2009). The results showed that after GAC treatment the wastewater toxicity had been reduced showing that the wastewater only required a 1:4 dilution (75% wastewater:25% water), thus allowing more wastewater to be treated at one time.

A pilot scale study to evaluate the removal efficiencies of pesticides in the pesticide production wastewater was completed. An MBR reactor was set up an opposed to a conventional activated sludge tank for the advantages as previously detailed in Section 2.3.5.1. After MBR the pesticide wastewater was treated in via two different ways, UV photolysis, or GAC and UV photolysis. The MBR-GAC pilot scale study showed the process to be very effective especially when nutrients and alkalinity, with total removal efficiencies increasing from 53% to 94%. The additional nutrients increased the use of recalcitrant pesticides as a food source when an adequate and balanced nutrient supply was provided. Additionally, there were increases in removal efficiencies for BOD from 50% to 72% and COD from 71% to 88%. GAC showed that after 1400 BV the pesticide concentrations were between 0.0-0.24 mg/L, which were significantly above the environmental quality standards (EQS) discharge limits, indicating that the GAC columns could be run for longer, reducing the frequency of regeneration. Moreover it can be seen that running at higher EBCTs increases the capacity of the GAC. Overall, the GAC experiments demonstrated this treatment option with at these initial concentrations was an efficient and reliable treatment option for treating this pesticide production wastewater and but would not comply with the required discharge limits.

The application of combining UV as a post treatment for the MBR and MBR-GAC hybrid system, the pesticide concentrations were further reduced with pesticide concentrations in the range of 0.01-0.04 and 0.000- 0.004 mg/L, respectively. Photolysis with UV showed promising results to replace the GAC, as the MBR-UV system achieved a total pesticides removal of 99-100%. The MBR-UV hybrid system generated an effluent with 5 µg/L MCPA, 1 µg/L MCPB, 7 µg/L MCPP, 22 µg/L PCOC, 39 µg/L 2,4-D, 0.75 µg/L 2,4-DP, 0.37 µg/L 2,4-DB, 5 µg/L 2,4-DCP and 5 µg/L 2,4,6-TCP. Nevertheless, even with high effectiveness of the MBR and UV system the effluent did not reach the discharge limits WFD annual average environmental quality standards (EQS) for 2,4-D (0.3 µg/L) and MCPA (2 µg/L), just the EQS for 2,4-DCP (20 µg/L) and MCPP (18 µg/L) would be met without the need of GAC. The EQS are set for environmental water quality and could be met if the treated wastewater is discharged to a water body that ensures 1:150 dilution, assuming that no 2,4-D is present in receiving water body.

6.1 References

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▌Conclusion

The performance of biological, physical and chemical treatment processes have been experimented individually and as part of a hybrid system.

Evaluating the results from the characterisation of the pesticide production wastewater, it can be seen that the wastewater contains;

- High variability between different batches of pesticide wastewater collected at different times
- High concentrations of COD (18675-47763 mg/L)
- A COD/BOD ratio of 3.08 indicating poor biodegradability
- High suspended solids (1437 mg/L) therefore it is recommended to implement a solids separation process
- Ratio between total suspended solids and volatile suspended solids indicates that the solids are mostly inorganic, also emphasizing the need for a solids separation stage.
- Low levels of nutrients; ammonium (19.1 mg/L) and phosphate (2.5 mg/L)
- Carbon:nitrogen:phosphate ratio of 22930:15:1, indicating for nutrients maybe required to heighten the biological process
- A wide variation of pesticide concentrations from 0.1-107 mg/L

The results from biological, physical and chemical experiments showed that the pesticide production wastewater;

- Can be treated biologically be must be diluted to a 25% wastewater unless treated with GAC prior to biological treatment then the wastewater must be diluted to 75% wastewater
- Adding nutrients (NH_4 - 1.7 g/L, PO_4 – 0.23 g/L) and alkalinity (0.1 g/L) improves the biological performance and increases pesticide removal efficiencies and prevents accumulation of 2,4-DB.
- Anaerobic biodegradability tests presented an inefficient process for removing pesticides, as the wastewater was toxic to anaerobic digested sludge microorganisms up to 1% wastewater; therefore this line of work was regards as not economically viable and was not pursued.

- Batch tests using GAC show good adsorption of pesticides. Batch test showed that most of the pesticides have equilibrium times within 5 hours and 58-100% pesticide removal was observed within 24 hours.
- Column tests completed showed GAC regeneration was required between 599-1374 bed volumes when using 3-30 minutes EBCT. The GAC experiments demonstrated this treatment option to be a very efficient and reliable treatment option for treating this pesticide production wastewater.
- AOPs (Fenton process and UV/H_2O_2) were not suitable for treating this specific pesticide production wastewater. Studies carried out show that adding H_2O_2 reduces the pesticide removal levels by filtering the UV light. It is clear that the pesticides in this study are able to be degraded with total pesticide removal of 50% by utilising UV alone at an intensity of 30 W/m^3.

The results from hybrid experiments showed that;

- The effluent from the GAC in the GAC-biological hybrid system was not toxic to aerobic microorganisms at 75% wastewater that GAC treatment whereas prior to GAC treatment the pesticide wastewater was toxic to microorganisms above 25%. However after 552 BV of GAC and biological treatment removals efficiencies were low with phenoxy acids, dichloro acids and 2,4,6-TCP been 37, 76 and 30%, respectively.

- The MBR-GAC pilot scale study showed the process to be very effective especially when dosing with addition nutrients (1.7 g/L NH_4 and 0.23 g/L PO_4) and alkalinity (0.1 g/L), with total removal efficiencies increasing from 61% to 81%. The addition of nutrients and alkalinity increased the use of recalcitrant pesticides as a food source when an adequate and balanced nutrient supply was provided. Furthermore there were increases in removal efficiencies for BOD from 50% to 72% and COD from 71% to 88%. GAC showed that after 1140 BV the pesticide concentrations were between 0.03-10.3 mg/L, which were significantly below the EQS discharge limits, indicating that the GAC columns could be run for longer, reducing the frequency of regeneration. Also it can be seen that running at higher EBCTs increases the capacity of the GAC.

- When combining UV as a post treatment for the MBR and MBR-GAC hybrid system, the pesticide concentrations were reduced further to pesticide concentrations between 0.29-0.61 and 0.29- 0.76 mg/L, respectively. Suggesting that a MBR and UV system was adequate to reach the discharge limits without the need of GAC.

For the pesticide production wastewater under investigation the final discharge effluent limits are set by the environmental quality standards (EQS) which are 7.1 mg/L (2,4-D), 73 mg/L (2,4-DCP) 219 mg/L (MCPP) and 70.2 mg/L (MCPA) for discharge to sewer (Scenario 1a); 5.2 mg/L (2,4-D), 30 mg/L (2,4-DCP) 158 mg/L (MCPP) and 161 mg/L (MCPA) for discharge to sewer (Scenario 1b) and 6.1 mg/L (2,4-D), 62 mg/L (2,4-DCP) 187 mg/L (MCPP) and 108 mg/L (MCPA) for discharge to a river (Scenario 2). Therefore all hybrid processes above are all effective treatment processes that would comply with all scenarios to meet the required discharge limits.

As a recommendation, further work should be completed to determine the CAPEX and OPEX, in order to determine which process is the most economical and feasible treatment process.

Appendix A– UV/H_2O_2 Experiments

The pesticide removal using UV and UV/H_2O_2 after 60 minutes irradiation time with a UV intensity of 2 mW/cm^2 in pesticide production wastewater showed total pesticide were removed by 38% (UV) and 35% (UV/H_2O_2) (Figure 8-1 top). The addition of H_2O_2 at 1250 mg/L showed no advantage in removal of pesticides with UV and UV/H_2O_2 with average pesticides removal of 24% and 23%, respectively (Figure 8-1 top). The compound with the higher percentage removal was 2,4-D with UV (92%) and UV/H_2O_2 (91%). Hydrogen peroxide has been seen to improve the efficiency of pesticide removal. Kowalska et al. (2004) investigated the removal of pesticide 2,4-D using UV/H_2O_2 at pilot scale and was able to remove 2,4-D by 95% with initial concentration at 65 µg/L. James et al. (2014) observed removal levels >97% for MCPP and 2,4-D with initial concentration of 0.001 mg/L using a dose of 3 mg/L H_2O_2. However this was not observed in this study. This could be caused by other compounds such as organic matter in the wastewater contributed to the high strength, therefore a larger dose of H_2O_2 might be needed. Nevertheless, at high concentrations of H_2O_2, peroxide itself has been reported to scavenge free radicals (·OH) causing lower levels of pesticide degradation (Stocking et al.,2011; Wu & Linden, 2008).

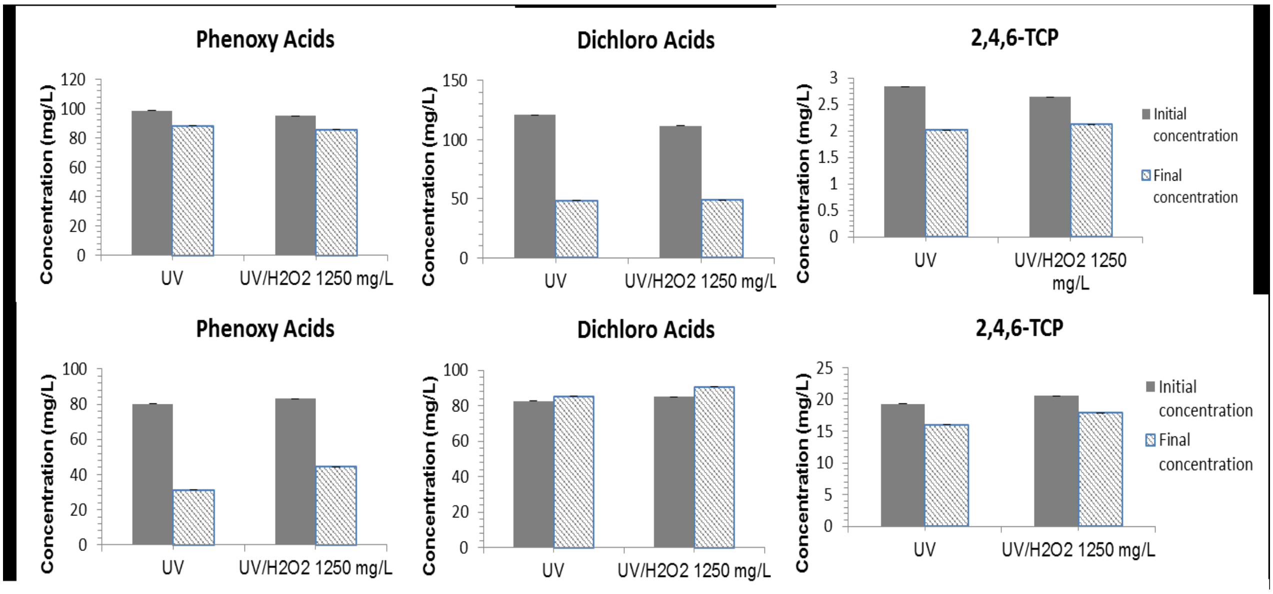

Figure 8-1. Initial and final concentration of pesticides after treatment with UV and UV/ H2O2 in the pesticide production wastewater at 2 mW/cm2 (top figures) and synthetic pesticide solutions at 2 mW/cm2 (bottom figures). Phenoxy acids

include MCPA, PCOC, MCPP and MCPB. Dichloro acid include 2,4-D, 2,4-DB, 2,4-DP and 2,4-DCP.

To determine whether other compounds in the wastewater affected the UV/H_2O_2 efficiency, the same experiment was repeated using a synthetic pesticide solution (Figure 8-1 bottom). The results showed total pesticide removals (phenoxy acids, dichloro acids and 2,4,6-TCP) were 30% (UV) and 19% (UV/H_2O_2) suggesting that UV alone can remove pesticides, especially for phenoxy acids (Figure 8-1 bottom). Nevertheless, the removals were much lower than the expected values. These results, similarly to the Fenton results, seem to indicate that chlorides in the wastewater (real and synthetic) maybe interfering with the H_2O_2 mode of action and radicals formation, reducing its efficacy. However chloride tests showed chloride concentration were 5 mg/L and remained as this concentration throughout the process therefore this hypothesis can be ruled out.