Investigation into an Adsorption and Electrochemical Regeneration Process for the Treatment of Two Trace Level Pesticides

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Submitted in total fulfilment of the requirements of the degree of MSc (by research)

Environmental Science

September 2017

Lancaster Environment Centre

The University of Lancaster

Confidentiality

Since some of the findings resulting from this project may lead to further process development or intellectual property protection, Arvia Technology Ltd request that this dissertation remains confidential for as long as possible.

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Abstract

The presence of organic micro-pollutants in aquatic systems and drinking water is of concern in most highly populated regions of the planet. Extensive surveys of major river systems in Europe and the United States have measured a wide array of organic contaminants including industrial chemicals, surfactants, pharmaceuticals and pesticides. The European Union's Water Framework Directive – aimed at achieving good environmental quality of surface waters at the catchment level - has a series of environmental quality standards that must not be exceeded for a wide range of water pollutants, including pesticides and other organic contaminants.

To meet these demands and challenges of higher water quality, Arvia Technology Ltd. have developed a novel water treatment process known as the Arvia™ Process. The Arvia Process combines adsorption with *in-situ* electrochemical regeneration which leads to the electrochemical oxidation of the adsorbed organic contaminant. The aim of the present study was to test the individual stages of the Arvia Process, namely adsorption and electrochemical regeneration of the proprietary adsorbent Nyex™, for its ability to remove and treat two current-use pesticides, atrazine and pirimicarb, at trace level concentrations.

Initial adsorption kinetic and isotherm studies indicated that the adsorbent, Nyex, could successfully remove both atrazine and pirimicarb when dissolved in water. This indicated that atrazine and pirimicarb could therefore potentially be removed using a combined adsorption and electrochemical process. During electrochemical regeneration of the adsorbent, ideally the adsorbed organic contaminant should remain adsorbed onto the sorbent and be fully oxidised to H_2O, CO_2 and inorganic ions. However, in the present study during electrochemical regeneration, adsorbate molecules desorbed from the Nyex surface and were subsequently transferred back into solution. However, some treatment was observed as evidenced by the formation of degradation products. Two atrazine degradation products were formed and were tentatively identified as deethyl-deisopropyl-atrazine and 4-ethylimino-6-isopropylamino-*s*-triazine. One pirimicarb degradation product was formed and was tentatively identified as 2-methylamino-5,6-dimethylpyrimidin-4-yl-dimethylcarbamate. Since there were only slight modifications to the structures of the original parent compounds, this indicated that the compounds were only partially oxidised. This may be the result of indirect electrochemical oxidation in the liquid phase as during this study there was desorption of the pollutants.

This investigation revealed that under the experimental conditions used in the present study electrochemical oxidation could not effectively remove and treat atrazine and pirimicarb at trace level concentrations. The experimental conditions used were likely responsible for the desorption of atrazine and pirimicarb thereby making the assessment of the performance of the system difficult. Future work should consider investigating the present methods under other experimental conditions to improve the treatment and destruction of atrazine and pirimicarb.

Declaration

I hereby declare that this dissertation is the result of my own original work and that no part of it has been presented for another degree in this university or elsewhere. I declare that due acknowledgement has been made in the text to all other material used.

Acknowledgements

Foremost, I would like to extend my thanks to Prof. Crispin Halsall for providing me with a great opportunity to carry out this industry-linked masters. I wish to thank him for being supportive and providing me with encouragement and motivation to meet the set goals. I would also like to take this opportunity to thank the members of the Arvia Technology team. The Arvia team has been very welcoming, kind and I have really enjoyed working with everyone. I wish to acknowledge Dr. Nigel Brown and Dr. Akmez Nabeerasool for their support, guidance and enthusiasm. Finally, a special thanks should be made to Dr. Claudia Moeckel for her time and help in assisting me to develop my analytical skills using the HPLC/MS.

Abbreviations

Abbreviation	Description
$^{-}$OH	Hydroxide Ions
·OH	Hydroxyl Radical
AC	Activated Carbon
ACN	Acetonitrile
AKE	Adsorption Kinetic Experiment
AOP	Advanced Oxidation Process
APA	Analyte Peak Area
BTC	Break Through Curve
C	Carbon
CS	Calibration Standard
DAD	Diode Array Detection
DI	Deionised water
EPA	Environmental Protection Agency
EQS	Environmental Quality Standards
EU	European Union
FG	Functional Group
GAC	Granular Activated Carbon
GIC	Graphite Intercalation Compound
GIC	Graphite Intercalation Compound
H	Hydrogen
HB	Hydrogen Bond
HPLC	High Performance Liquid Chromatography
IS	Internal Standard
ISPA	Internal Standard Peak Area
LC	Liquid Chromatography
m/z	Mass-to-Charge
MP	Micro-pollutant
MQ	Ultra-pure water
MS	Mass Spectrometer
N	Nitrogen
N_2	Nitrogen Gas
NOM	Natural Organic Matter
O	Oxygen
PAC	Powdered Activate Carbon
PS	Priority Substance
QC	Quality Control
RG	Regression Co-efficient
RO	Reverse Osmosis
RP	Reverse Phase
RT	Retention Time
SPE	Solid Phase Extraction
T	Trial
TOC	Total Organic
TSA	Total Surface Area
US	United States
WWTP	Wastewater Treatment Plant

Chapter 1 – Introduction

1. Micro-pollutants

1.1. Anthropogenic Chemical Pollution of Water Resources

The demand on our clean water resources is growing with the rapid and extensive increase in human population and economic growth. Loos et al., (2009) reported that of the Earth's accessible renewable freshwater, more than one third is used for agricultural, industrial and domestic purposes. This large amount of water used, driven by human development and unrestricted activities, is responsible for the increase in contamination of our water sources with numerous synthetic organic compounds (Schwarzenbach et al., 2006). As water is our most vital resource it is crucial to protect our water sources from anthropogenic pollution for the preservation of human and ecological health as well as the environment.

In the last 30 years, the European Union (EU) and United States (US) have registered circa 100,000 different synthetic organic compounds for commercial use (Loos et al., 2009). The production of these different synthetic compounds has been attributed to the high living standards of today's society and are responsible for advances in health care, sanitation, agriculture and industry. However, the EU reports that between 2004 and 2013, 42 % (almost half) of the combined total production of chemicals, were environmentally harmful compounds (European-Commission, March, 2016). The major concern is that a large (but unknown) quantity of these chemicals will disperse and persist in the environment and reach water bodies in mixtures alongside their degradation products (DPs) with unknown long-term effects on humans and the environment (Brack et al., 2017).

This has led to many different types of synthetic compounds ending up in many bodies of water at concentration levels below the mg/L range. The chemicals detected in water that fall below this range are termed "micro-pollutants" (MPs). Some MPs have become ubiquitous in natural water sources and have been detected in remote environments far removed from industrial areas. This demonstrates their ability to distribute themselves and persist in the environment (Loos et al., 2009). Consequently, much effort has been invested to evaluate the occurrence, fate and eco-toxicity of these MPs in the environment including in surface, ground and waste water (Schwab et al., 2005,

Schwarzenbach et al., 2006, Snyder, 2008, Pal et al., 2010, Lapworth et al., 2012, Luo et al., 2014, Barbosa et al., 2016).

1.2. Occurrence and Sources of Organic Micro-pollutants

The presence and occurrence of MPs in the environment has been reported in many publications, increasing concern in the scientific community and the general public. This creates a new challenge for the scientific community as MPs consist of a wide variety of synthetic and natural compounds. These include compounds such as pesticides, industrial compounds, pharmaceuticals, steroid hormones, personal care products and many more (Ribeiro et al., 2015). These synthetic and natural compounds exhibit a wide range of different chemical structures, functional groups (FGs) and physiochemical properties complicating the understanding of their behaviour, persistence and impact on the environment. Furthermore, most MPs are only present in water at trace level concentration ranging from a few ng/L to several µg/L. The diversity of MPs alongside their individual physiochemical properties and their low-level concentrations in the environment, make their detection, analysis and treatment complex (Luo et al., 2014).

The occurrence of MPs in surface water is often as a result of water discharge from waste water treatment plants (WWTPs) following incomplete removal. These WWTPs are not designed or tailored to remove and eliminate MPs (Kim et al., 2007, Benotti et al., 2009, Kock-Schulmeyer et al., 2013). Therefore, many of these MPs can pass through conventional waste water treatment processes. Since many of these MPs are known to be persistent and recalcitrant in nature, they're continuously reintroduced into the environment. This results in the most persistent of these compounds remaining in the aquatic environment threatening wildlife and ending up in our drinking water (Coupe and Blomquist, 2004, Kim et al., 2007, Snyder, 2008, Benotti et al., 2009, Kumar and Xagoraraki, 2010, Padhye et al., 2014).

Whilst the incomplete removal of MPs from WWTPs is a major pathway for the introduction of MPs to surface water, other sources include runoff from agricultural fields, livestock and aquaculture, landfill leachates, urban runoff and domestic and hospital effluents (Barbosa et al., 2016). The many different pathways MPs may follow are shown in Fig. 1.

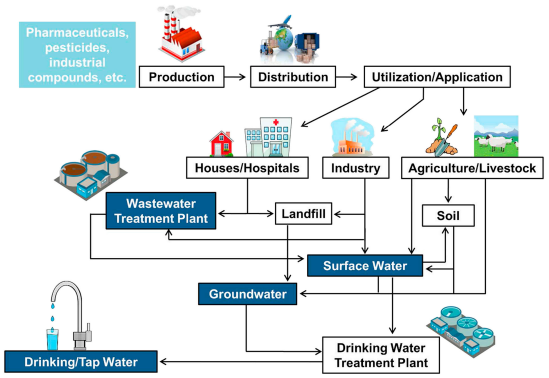


Fig. 1. Representative sources and routes of MPs in the environment (Barbosa et al., 2016).

1.3. Consequences

MPs which comprise of compounds such as pesticides and herbicides (biocides), pharmaceuticals including hormones and illegal drugs are all designed to have a biological effect. In the case of biocides, they're intrinsically designed to be hazardous and toxic to living organisms. The nature of these compounds and their effects evoke concerns regarding their ability to be unsafe, harmful and toxic to non-target organisms (Hernandez et al., 2013). However, it is a difficult task to assess the effects that many synthetic and natural trace level compounds, which may only be present in water at concentrations ranging from pg/L to µg/L, will have on the aquatic environment and human health (Schwarzenbach et al., 2006).

Overall studies done in many countries have reported, when comparing MP concentrations in the environment with their corresponding predicted no effect concentrations (PNECs), that most of the compounds were determined to be at concentrations without a) toxicological risk to human health and b) potential environmental significance (Schwab et al., 2005, Snyder, 2008, Luo et al., 2014). However, important to note is that these determined PNEC values were based on individual compounds instead of mixtures of contaminants such as is encountered in the aquatic environment. Furthermore, DPs of many MPs are still unknown and were not monitored in these studies (Luo et al., 2014). Despite many studies on the fate and toxicity of the parent MPs in the environment, there are research gaps causing uncertainty regarding human and eco-toxicological potential of DPs. This indicates that research should be continued in regard to understanding the health effects of these MPs especially in regard to their mixtures and DPs (Schwarzenbach et al., 2006).

1.4. Regulation

The preservation of our water from chemical contamination to assure its high quality is a major societal goal in the EU. The Water Framework Directive (WFD) alongside its daughter directives are the major body of legislation that establish a legal framework to protect and restore clean water across Europe and ensure its long-term and sustainable use (Brack et al., 2017). In 2000, the European Commission (EC) implemented the WFD with the aim of ensuring that all water bodies (rivers, lakes, coastal waters and ground water) achieve a "Good Ecological Status" by 2027. This means that bodies of water should contain only minimal pollutants to protect the integrity of vulnerable ecosystems to provide a natural habitat for animals and plants (UFZ, February 27, 2017).

The main pieces of legislation for the protection and sustainable use of European freshwater resources are:

- The Water Framework Directive

This was the first EU-wide push towards a clean water policy. Defined by the Directive 2000/60/EC, the Directive set forth a strategy with the aim of identifying substances as high priority substances (PSs) in their relation to being harmful to the aquatic ecosystem (Ribeiro et al., 2015).

- 2008/105/EC Environmental Quality Standards Directive

In this directive, a list containing 33 PSs was establish in 2008 by the EU in the field of water policy. For these 33 PSs and 8 other environmental contaminants, Environmental Quality Standards (EQSs) were defined. These EQSs were based on available data of acute and chronic effects to the aquatic environment and human health (Ribeiro et al., 2015).

The 2000/60/EC and 2008/105/EC Directive was amended by the:

- 2013/39/EU Directive

This updated water framework policy contains the latest amendment of the list of PSs. This directive has now 45 PSs which calls for the enhanced monitoring of these compounds and for various options for their treatment (Barbosa et al., 2016). This directive also promotes preventative action and the

"polluter pays" principle and dealing with emissions of pollutants at the source. Furthermore, due to the high detection levels of MPs in the environment and the inability of WWTPs to eliminate and remove these compounds, the directive aims to promote and support the development and research towards new water and waste water treatment technologies (Ribeiro et al., 2015).

This legislation has been responsible for the extensive monitoring of the chemicals described in the directives in all EU Member States (Brack et al., 2017).

1.5. Micro-pollutants to be Investigated in this Research Work

Synthetic pesticides have been widely employed since the 1940s (Unsworth, 2010) and they have contributed to the high living standards of today's society and greatly benefited humans by assuring high quality food products and controlling infectious diseases among others. However, even at low concentrations, unintended exposure to pesticides may have adverse effects and implications on human health (Mostafalou and Abdollahi, 2013, Kim et al., 2017). Furthermore, the long-term and excessive use of pesticides in areas of intensive agriculture have led to environmental contamination (Parron et al., 2014).

The agricultural sector is the largest consumer of pesticides accounting for around 85 % of the world's production. In 2006 and 2007, approximately 2.4 million tonnes of pesticides were used world-wide each year. Within this figure, herbicides made up the largest portion of the total use of pesticides and was followed by other pesticides and insecticides. Today herbicides continue to be the most common type of pesticide used in agriculture (Parron et al., 2014).

Although the largest portion of pesticide use is attributed to agriculture, pesticides are also used to maintain golf courses, parks, gardens and major roads (Kim et al., 2017). This highlights that the potential of pesticide exposure is not only considerable to occupational workers, but also to the public. Direct exposure to pesticides occurs predominantly from occupational, agricultural and household use (Kim et al., 2017), while the most common sources of indirect exposure to the public include drinking water, food, dust and air (Parron et al., 2014). The increased risk and potential for pesticide exposure is largely dominated by the pesticide's physical and chemical properties (Kim et al., 2017).

Similarly, The physical and chemical properties of pesticides dictate their behaviour and lifespan in the environment. As pesticides are designed to be toxic and in some cases persistent, they may be hazardous or give rise to concerns once present in the wider environment. For example, the environmental problems of the older generation organochlorine insecticides like DDT, aldrin and chlordane are now well documented (Unsworth, 2010).

It has been established that the use of pesticides has detrimental impacts on human health and ecological systems (Kim et al., 2017). In relation to human health, studies are reporting mounting toxicological evidence which suggests that pesticide exposure is linked to various serious diseases. These include: various types of cancer such as lung (Shaukat et al., 2013, Lerro et al., 2015b), breast (Rivero et al., 2015, Lerro et al., 2015a) and thyroid (Lerro et al., 2015a), brain tumours (Provost et al., 2007, Samanic et al., 2008), leukaemia (Van Maele-Fabry et al., 2011, Bailey et al., 2015), diabetes (Jaacks and Staimez, 2015) and Parkinson's disease (James and Hall, 2015, Brouwer et al., 2015). In some specific cases *N*-methylcarbamates, a main group of insecticides, were demonstrated to have carcinogenic potential (George and Shukla, 2011, Alavanja and Bonner, 2012) and in the US, an increased risk of lung cancer was observed among herbicide users dispersing acetochlor/atrazine product mixtures versus non-users (Lerro et al., 2015b).

As stated by Kim et al., (2017) "On the basis of scientific evidence, the real, predicted, and perceived risks that pesticides pose to human health (occupational and consumer exposure) and the environment are justified". As a result, the use and application of pesticides is frequently reviewed and certain chemicals have been restricted and banned in the UK and EU (Commission E. Review, Annex I of Directive 91/414/EEC). Additionally, drinking water standards for the maximum permitted concentration, for any individual pesticide, has been set by the EU at 0.1 µg/L (WFD, 2006).

The two pesticides, atrazine and pirimicarb, were chosen for this study based on their current or recent use across the EU and North America, contrasting physical-chemical properties and the ease with which they fall into a pre-existing analytical methodology.

1.5.1. Atrazine

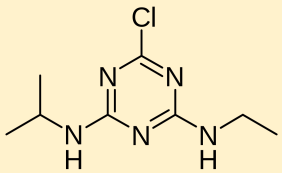
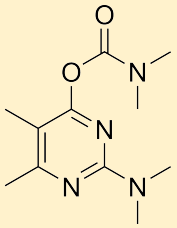
Atrazine is a selective triazine herbicide that is used in agriculture as well as on recreational and residential areas. Today atrazine is one of the most commonly used pesticides in the world including

the US and Australia (Government, 2016). Based on survey data from 2000 to 2010 the US Environmental Protection Agency (EPA) have reported that annual usage in the US was approximately 33,000,000 kg of active ingredient for 71,000,000 acres (Agency, 2013). Atrazine is a very stable compound having a low biodegradability and consequently a long half-life in surface water (>200 days) (Services, 2003, ATSDR, 2003). Furthermore, it has a relatively low adsorption onto soil and is slightly soluble in water (33 mg/L at 22 °C) making atrazine a mobile compound in the environment. As a result, atrazine has become a ubiquitous and chronic water pollutant with increasingly significant concerns over wide spread drinking water contamination (Coupe and Blomquist, 2004, Luo et al., 2014, Padhye et al., 2014). This has led to the application and use of atrazine being banned in the EU and atrazine has been included on the priority list of the Water Framework Directive (Directive 2000/60/EC) in the EU.

1.5.2. Pirimicarb

Pirimicarb is also widely used in agriculture but as a selective carbamate insecticide for aphid control on crops. In the UK, from 2012 to 2015, almost 100,000 kg of the active ingredient was administered onto crops (FERA). Pirimicarb is highly soluble in water (2700 mg/L at 25 °C) making it a highly mobile compound. As a result, traces of pirimicarb have been detected in surface water (Moschet et al., 2014). Pirimicarb is not as persistent in the environment as atrazine. However, it is a pseudo persistent chemical due to its continuous low level introduction into the environment. The US-EPA have classed pirimicarb as a moderately persistent chemical in the environment (EPA, 1999).

The physio-chemical and toxicological properties of atrazine and pirimicarb are shown in Table 1 (EPA, 2005, EPA, 1999, Gupta et al., 2011).

Table 1. Physio-chemical & toxicological properties of atrazine and pirimicarb		
Pesticide	**Atrazine**	**Pirimicarb**
Molecular structure		
Molecular formula	$C_8H_{14}ClN_5$	$C_{11}H_{18}N_4O_2$
Molecular weight	215.69	239.29
Chemical family	Organochlorine	Carbamate
Pesticide type	Herbicide	Insecticide
Solubility in water (25°C)	33 mg/L	2,700 mg/L
Log octanol – water partition coefficient (Log K_{ow})	2.6	1.7
Conjugate Acid Dissociation Constant (pK_{ah})	1.7	4.4
Environmental fate	Moderately persistent and mobile, low bio-accumulation potential	Moderately persistent and mobile, low bio-accumulation potential
Carcinogen class	Class C (Suggestive Evidence of Carcinogenic Potential)	Class B (Likely to be Carcinogenic to Humans)
Toxicity class	I (Highly toxic)	II – III (Slightly to moderately toxic)
Use classification (US)	Restricted and banned	In Use
Use classification (EU)	Banned since 2004	In Use
WFD drinking water limit (EU)	0.1 µg/L	0.1 µg/L
On the WFD list of Priority Substances (EU)	Yes	No

2. Water and Wastewater Treatment

2.1. Advanced Water Treatment Technologies

Rapid growth in agriculture, industry and urbanization is responsible for the release of huge amounts of harmful and toxic MPs (including pesticides) into surface waters (Benotti et al., 2009, Moschet et al., 2014, Luo et al., 2014). Many of these synthetic pesticides released into the environment are chemically stable compounds making them resistant to degradation and enabling them to persist in the environment. This has led to the implementation of stringent regulations and policies by regulatory bodies in countries all over the world including China's Ministry for Environmental Protection, the US-EPA and the WFD in the EU.

If tolerable pesticide concentrations in drinking water are not met through the control of key sources (e.g. better management of agricultural use) and treatment through conventional WWTPs, then advanced water treatment will be required to ensure that water standards are met. Consequently, there has been a rise in advanced technologies aimed at removing trace level MPs during both drinking water and wastewater treatment. Techniques of growing relevance include chemical methods such as advanced oxidation processes (AOPs) and physical methods such as micro-and ultra-filtration, reverse osmosis (RO) membranes and adsorption. These are successful chemical and physical methods used to remove MPs from water however, each method has its own constraints and disadvantages like high operational costs and disposal problems.

2.2. Types of Advanced Water Treatments to Treat Micro-pollutants

Advanced water treatment technologies can be classified into three different categories: biological, chemical and physical processes. Here the focus will be on the chemical and physical processes. In regard to the treatment of pesticides in water, many advanced chemical and physical water treatment processes have been investigated and used.

2.2.1. Advanced Chemical Water Treatment Processes

Advanced chemical water treatment methods include the use of AOPs. There are several methods used in AOPs to treat water which include ultraviolet (UV) radiation, ozone (O_3), hydrogen peroxide (H_2O_2) and molecular oxygen (O_2). Examples of some AOPs used for the treatment of pesticides are: UV/H_2O_2, UV/O_3, TiO_2/UV, Fenton and photo-Fenton and electrochemical oxidation (Martin-Gullon and Font, 2001, Malato et al., 2002, Perez et al., 2006, Sanches et al., 2010, Borras et al., 2010, Zaviska et al., 2011). However, the most common AOPs are the Fenton process, heterogeneous photo-catalysis, ozonation and electrochemical oxidation (Ribeiro et al., 2015).

The aim of AOPs is to remove recalcitrant organic contaminants from water through the mineralisation of these compounds. By mineralising these compounds they are converted into less harmful or at least into more biodegradable compounds. Total mineralisation yields end products such as CO_2, H_2O and inorganic ions and therefore AOPs are considered to be a clean technology (Anglada et al., 2009, Ribeiro et al., 2015). On a fundamental level the concept of all AOPs is the production of hydroxyl radicals (·OH), which will attack the organic contaminant. How efficient the AOP is, is contingent on the amount of ·OH radicals formed. ·OH radicals indiscriminately attack and degrade organic contaminants as they are highly reactive and unselective oxidising agents (Ribeiro et al., 2015).

One of the major disadvantages of AOPs can be incomplete mineralisation leading to the formation of oxidised DPs, which may be more persistent and/or toxic than the original compound. In which case, post treatment will be required to safely remove these oxidised compounds before disposal of the contaminated water (Ribeiro et al., 2015). However, the extent of research work conducted in this field highlights that there is a promising potential for AOPs to completely degrade these pesticides and other anthropogenic organic contaminants from contaminated water.

2.2.2. Advanced Physical Water Treatment Processes

Physical methods for the treatment of pesticides in water include: micro- and ultra- filtration (MF and UF) membranes, RO membranes and adsorption. Although MF and UF have been proven to be successful at removing larger industrial compounds from industrial effluents, often the size of the membrane pores are not small enough to block MPs from passing through (Luo et al., 2014). In contrast, RO membranes are highly effective at removing MPs and are used for the purification of

water (Sharma and Bhattacharya, 2017). This is an eco-friendly technique that does not use any chemicals and can effectively remove most types of organic contaminants including inorganic compounds, organic compounds like pesticides and microbes. The disadvantages of such a technique are that the purified water is stripped of useful minerals (Sharma and Bhattacharya, 2017). Also the low permeability of the membrane will require high pressures and consequently high energy consumptions (Van der Bruggen et al., 2003).

Alternatively, the use of adsorbents has been proven to provide a straightforward, cleaner and more effective approach to treating water. Adsorption is a process in which the dissolved organic contaminant adheres to the surface of a solid particle due to hydrophobic and electrostatic interactions between the adsorbent and adsorbate (Nam et al., 2014). The most commonly used adsorbent for water treatment is activated carbon (AC) due to its high adsorption capacity resulting from its high internal surface area and porosity. AC is a versatile adsorbent, capable of treating a wide range of effluents and effectively removing pesticides even at trace levels from water (Gupta et al., 2011, Moussavi et al., 2013).

2.3. Arvia's Solution - The Arvia Process

Arvia Technology Ltd. have coupled one of the most widely used methods for advanced water treatment, adsorption, with an AOP, electrochemical oxidation. Where the electrochemical regeneration (ERG) of the adsorbent is responsible for the *in-situ* electrochemical oxidation of the adsorbed organic species. This innovative combination of simultaneous adsorption and ERG with *in-situ* electrochemical oxidation has been shown to effectively remove and treat organic contaminants dissolved in water (Brown et al., 2004a, Asghar et al., 2012) including metaldehyde, a commonly used pesticide (Nabeerasool et al., 2015). This technology and process, for the treatment of contaminated water, is called "The Arvia Process".

The process depends on:

1) The adsorbent, called Nyex
2) A continuous adsorption and *in-situ* regeneration process of the Nyex

Nyex is a graphitic carbon-based adsorbent, which has been patented by Arvia Technology Ltd. It is non-toxic, non-porous and a highly electrically conducting material. The non-porosity of the Nyex facilitates rapid pollutant adsorption, while its conducting nature allows for rapid ERG. This restores the adsorptive capacity of the Nyex while simultaneously electrochemically oxidising and destroying the adsorbed pollutant. This is a big advantage over other adsorbents such as GAC, which once exhausted must be discarded by either landfill or incineration, making the Arvia Process an environmentally friendly and inexpensive solution (Jeswani et al., 2015). A wide range of organic pollutants have also been shown to be successfully treated using this technology including dyes, pesticides and herbicides (Brown et al., 2004a, Asghar et al., 2012, Nabeerasool et al., 2015).
Thus, as a result, the Arvia Process of adsorption combined with ERG, that uses the proprietary adsorbent - Nyex, is now being commercialised by Arvia Technology Ltd. for the treatment of wastewater.

The present study aims not to test the Arvia Process itself, but the individual stages of the process i.e.: adsorption and ERG of the Nyex. This is necessary to gain scientific understanding of the underlying principles of the Arvia Process. Furthermore, the objective of this study was to gain an insight into the adsorption performance/mechanism of the Nyex and the ERG of the Nyex when using trace level MP concentrations.

3. Adsorption and Electrochemical Regeneration

3.1. Adsorption

In the process of adsorption, molecules of a solute (adsorbate) distribute themselves between two phases, a liquid or a gas phase and a solid phase (adsorbent) (Hussain, 2012). This adsorbate distribution between the two phases is due to a complex interplay of non-electrostatic and electrostatic forces between the adsorbate and the adsorbent (Moreno-Castilla, 2004). Therefore, adsorption is a surface phenomenon (Gupta et al., 2011). Adsorption however, can also be viewed as an exchange process, whereby molecules adsorb not only because they're attracted to the adsorbent, but also because the solution may reject them (Moreno-Castilla, 2004).

Depending on the nature of the interaction of the adsorbate and the two phases, physical or chemical adsorption may occur. Non-electrostatic interactions in the liquid phase between the surface of the adsorbent and adsorbate are responsible for physical adsorption. These interactions are always attractive and include van der Waal's forces, H bonding and hydrophobic interactions. These are

relatively weak forces and so physical adsorption is readily reversible whereby the adsorbed species are released back into solution (desorption) (Moreno-Castilla, 2004).

Whereas in chemical adsorption, electrostatic interactions can be either attractive or repulsive and can strongly bind the adsorbate molecules to the surface of the adsorbent (Ho and McKay, 1998). These interactions occur when the adsorbate molecule is protonated or dissociated in the aqueous solution and chemical bonds, formed through the exchange or sharing of electrons on the surface of the adsorbent and adsorbate, bind the adsorbate to the adsorbent (Moreno-Castilla, 2004, Ho and McKay, 1998).

Adsorption is used for the treatment of drinking water, waste water and it has applications in the chemical, pharmaceutical, food and beverage industries. It is a method that is fast, efficient, inexpensive and capable of removing a wide range of chemicals (Westerhoff et al., 2005, Nam et al., 2014).

Adsorption of organic contaminants from the liquid phase onto an adsorbent are influenced by several factors. These include (Dabrowski et al., 2005):

- The characteristics of the adsorbent – texture and porosity, surface area and surface chemistry (resulting from the FGs present on its surface)
- The characteristics of the adsorbate – presence of FGs, pKa, molecular weight and solubility
- The conditions of the solution – pH, ionic strength, temperature, adsorbate concentration and the presence of competing adsorbate molecules

3.2. Adsorption Isotherms

Adsorption is studied through adsorption isotherms which may be presented graphically. These graphs depict the relationship between the concentration of adsorbate in the liquid phase to its concentration on the surface of the adsorbent at equilibrium and a fixed temperature. Isotherm graphs are constructed by using fixed volumes of various known concentrations of adsorbate and exposing them individually to a fixed mass of adsorbent. These graphs allow for the evaluation of the capacity of the adsorbent for a particular adsorbate. Furthermore, the shape of the curve can be used to understand the adsorption mechanism occurring (Giles et al., 1960).

For the adsorption of organic solutes, Giles et al., (1960) classified isotherms into four main classes, according to the character of the slope of the initial portion of the curve. The four main classes are: i) L-shaped curves “Langmuir isotherms”, ii) S-shaped curves, iii) H-shaped curves “high affinity” and iv) C-shaped curves “constant partition” (Fig. 2.). Characterisation of the shape of the curve further from the origin leads to further sub-classification of the four main classes i.e.: shows the behaviour of the adsorbate/adsorbent equilibrium relationship at higher concentrations.

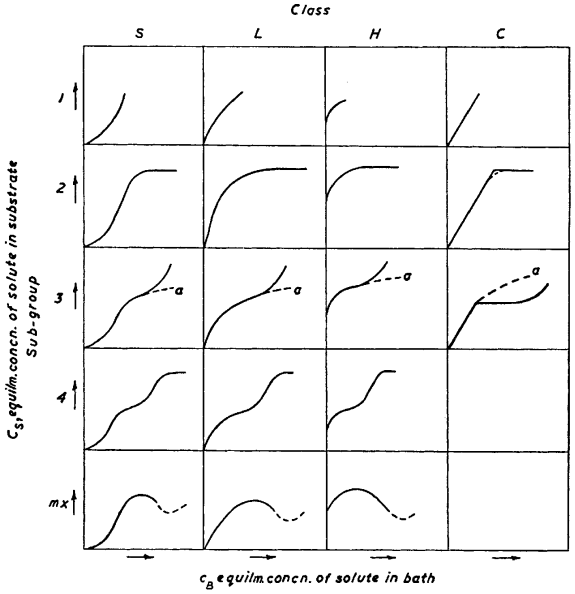


Fig. 2. Classification of isotherm shapes (Giles et al., 1960)

i) L – shaped curves

The initial slope of the curve (L-1) shows that as more adsorbate molecules are taken up by the active sites on the adsorbent, the harder it becomes for new solute molecules to find an available active site on which it can be adsorbed. Subsequently, higher concentrations allow for the further evaluation of the adsorptive behaviour of the adsorbate molecules. Thus, according to Giles et al., (1960), a long plateau (L-2) occurs if the mono-molecular layer of the adsorbate molecules have oriented themselves in such a way that the new surface is now less attracted to the adsorbate molecules. As a result, the slope of the isotherm gradually falls and reaches a plateau, as increasing adsorbate concentration has no effect on further adsorption of the adsorbate. However, if the adsorbate molecules in the mono-molecular layer are attracted to other adsorbate molecules in the liquid phase, multi-layer adsorption will occur, leading to an L-3 and L-4 curve. Organic molecules frequently exhibit Langmuir-type isotherms (Moreno-Castilla, 2004).

ii) S – shaped curve

Here the initial part of the curve has a steep incline. This suggests that the more solute already adsorbed, the easier it is for additional amounts to become attached. This indicates that there are molecular interactions between the adsorbed solute molecules (Giles et al., 1960).

iii) H – shaped curve

For H – shaped curves there is a high affinity of the solute molecule for the adsorbent, therefore the initial portion of the curve is vertical.

iv) C – shaped curve

A C – shaped curve is characterised by a straight line going from the origin, up until a point at which maximum adsorption has occurred and results in a sudden plateau (Hussain, 2012). This indicates that there is a constant distribution in the concentration of the adsorbate molecule in the liquid phase and adsorbed onto the adsorbent. This ratio, between the distribution of the adsorbate between the two phases, is known as a "distribution coefficient". These curves are typically observed with a porous adsorbent (Giles et al., 1960).

3.3. Adsorption Isotherm Models

There are various adsorption isotherm models which characterize the experimentally measured adsorption isotherms. These models can help establish and determine: the affinity the sorbate has for the sorbent, the adsorption mechanism and the surface properties of the adsorbent.

For organic contaminants, the models most frequently used to predict the empirical data are Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906).

3.3.1. Langmuir Isotherm Model

The Langmuir isotherm model makes the assumption that the surface of the adsorbent is homogeneous and that all the adsorption sites have equal adsorbate affinity. At equilibrium, a

saturation point is reached, in which no further adsorption occurs. At this point, the adsorbent will have complete mono-layer coverage (Langmuir, 1918). The Langmuir isotherm equation is defined as:

$$q_e = \frac{Q_0 K C_e}{1 + K C_e}$$

Where,

Q_0 represents the maximum monolayer adsorbent adsorption capacity (µg/g)

K is the Langmuir equilibrium constant (L/µg)

q_e is the amount of substance adsorbed onto the adsorbent (µg/g)

C_e is the equilibrium adsorbate concentration in the aqueous phase (µg/L)

3.3.2. Freundlich Isotherm Model

The Freundlich isotherm model is characterised by heterogeneous energy distribution and thus heterogeneous surface adsorption sites. Furthermore, unlike the Langmuir isotherm model, the Freundlich isotherm is applicable to both mono-layer and multi-layer coverage (Hussain, 2012).

Freundlich isotherm equation is defined as:

$$q_e = K_f C_e^{\frac{1}{n}}$$

Where,

q_e is the amount of substance adsorbed onto the adsorbent (µg/g)

C_e is the equilibrium adsorbate concentration in the aqueous phase (µg/L)

K_f is an indication of the adsorptive capacity of the adsorbent (L/g)

1/n is the Freundlich intensity parameter (a measure of the intensity of the adsorption)

3.4. Parameters affecting Adsorption

- Surface Chemistry

The surface chemistry of the adsorbent plays an important role and is crucial in adsorption. The presence or lack of chemical FGs will determine and affect the surface charge and properties of the adsorbent (Nkrumah-Amoako et al., 2014). This greatly influences the adsorption equilibrium time and adsorption capacity of the adsorbent.

- pH

The pH of a solution can affect the ionisation of the adsorbate and the ionisation of the FGs present on the surface of the adsorbent. This can lead to desirable and undesirable electrostatic effects. Furthermore, the pH can have an effect on the solubility of the adsorbate molecule and thus have a significant effect on its adsorption (Moreno-Castilla, 2004).

3.5. Electrochemical Oxidation

Electrochemistry is the study of the chemical reactions that take place at the interface of an electron conductor (metal electrode) and an ionic conductor (electrolyte). In these chemical reactions electron transfer occurs between the electrode and the electrolyte in solution. Thus, any chemical reaction in which electrons are transferred from an electrode to an electrolyte is called an electrochemical reaction (Asghar, 2011). In an electrochemical process this transfer of electrons from the electrode and electrolyte is driven by oxidation and reduction reactions (redox reactions). A redox reaction describes the transfer of electrons from a substance that is being oxidised to one that is being reduced. For every oxidation, there must be an associated reduction.

The electrochemical process which occurs in an electrolytic cell is one in which electrons are transferred from the anode to the cathode, making the anode temporarily positively charged. Thus, at the anode we have oxidation. The formation of electrons at the anode is from the oxidation of water (Hussain, 2012):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Subsequently, electrons from the anode are transferred to the cathode making it temporarily negatively charged. The cathode is reduced as it has gained electrons. Thus at the cathode we have reduction of water (Hussain, 2012):

$$2H_2O + 4e^- \rightarrow H_2 + 2OH^-$$

As water is consumed in this reaction, hydroxide ions (OH^-) will be created and hydrogen gas (H^2) will evolve at the cathode (Brown et al., 2004b).

The electrochemical process which occurs in an electrolytic cell is one which consumes energy. Thus there is an external power source which allows a current to pass from the anode to the cathode and controls the rate of the electrochemical reactions occurring in the cell. An electrolyte is placed in between the anode and cathode to complete the electric circuit, by allowing for the movement of ions through the electrolyte. With the introduction of a current, between the two electrodes, a voltage is established. This is called the cell potential and will indicate as to whether the reaction conditions are favourable or not (Asghar, 2011).

Electrochemical oxidation is a clean and powerful technique used for water treatment (Butkovskyi et al., 2014). In electrochemical oxidation, organic contaminants are broken down through direct and in-direct electrochemical oxidation. During direct electrochemical anodic oxidation, organic compounds are destroyed at the anode surface. Whereas, during indirect electrochemical oxidation, a strong oxidizing species is electrochemically generated and acts as a mediator to perform the oxidation. Thus, oxidation of the organic compound takes place in solution, rather than on the anode surface.
Many reports have demonstrated non-selective oxidation of organic compounds, including at trace levels, by these processes (Anglada et al., 2009, Radjenouic et al., 2011, Zaviska et al., 2011).
However, one of the main disadvantages of electrochemical oxidation is in its potential to produce halogenated or oxidised DPs (Butkovskyi et al., 2014) which can be more toxic and persistent than the original parent compound.

3.6. Electrochemical Regeneration

Adsorbents are a very popular technique used to remove organic contaminants from water. However, issues arise once these adsorbents are fully saturated with the organic contaminant. Disposal of spent adsorbents is environmentally undesirable and the thermal regeneration techniques (used on AC) account for high energy costs, 5 – 10 % material losses and off-site regeneration, resulting in high transportation costs (Hussain et al., 2013). Thus, problems concerning the regeneration of adsorbents for their re-use is a major issue.

The coupled approach of combining adsorption and ERG with *in-situ* electrochemical oxidation has been investigated as a substitute for thermal regeneration. In an electrolytic cell, electrochemical oxidation of the saturated adsorbent will: i) destroy any organic contaminants adsorbed by direct and in-direct anodic oxidation and *in-situ* ii) restore the adsorptive capacity of the adsorbent by the removal of the adsorbed species (Brown et al., 2004a). There are a number of advantages to this method including *in-situ* regeneration of the adsorbent, minimal adsorbent losses and it is a chemical free process (Jeswani et al., 2015).

However, there are some drawbacks to the ERG of adsorbents, which is dependent on the type of adsorbent used. AC adsorbents are not highly conducting electrical materials, this means that regeneration times would be long and consequently would require a high energy consumption. However, this problem can be eliminated by using a non-porous material like the Nyex. As described by Hussain et al., (2013), in an electrolytic cell ERG of the used Nyex generates relatively low voltages due to the highly conducting nature of the adsorbent. This means that the adsorbent can be regenerated very quickly with a low energy consumption (Brown et al., 2004b, Asghar et al., 2012).

One of the major drawbacks of adsorbents with low porosity, like Nyex, is that these adsorbents have a low adsorptive capacity. However, in contrast to AC, this means that the time to reach equilibrium is lower and so removal of the organic contaminants through ERG is quicker. Using this method, the Nyex has been shown to be capable of successfully removing a wide range of organic contaminants including pesticides (Brown et al., 2004a, Nabeerasool et al., 2015).

3.7. Degradation Products

There are two different pathways in which organic contaminants can be electrochemically oxidised during electrochemical oxidation (Anglada et al., 2009):

i) Electrochemical Conversion

Here organic contaminants are only partially oxidised, represented in equation 1, and subsequent treatment may be needed.

1)

$$R \rightarrow RO + e^{-}$$

ii) Electrochemical Combustion/Mineralisation

Here organic contaminants are transformed into carbon dioxide, water and other inorganic components, represented by equation 2.

2)

$$R \rightarrow CO_2 + H_2O + Salts + e^-$$

In order to achieve a comprehensive treatment of the adsorbed organic contaminant, the organic compound would have to be mineralised into CO_2 and H_2O, during ERG. Incomplete oxidation of the adsorbed organic contaminant could lead to the formation of various undesirable DPs.

In studies conducted by Brown and Roberts, (2007), it was initially speculated that the adsorbed organic contaminant was either i) completely oxidised, forming no DPs or ii) that the DPs formed were retained on the adsorbent during ERG and being further oxidised. But recent studies, performed by the same group, have shown that intermediate oxidation products were formed during the ERG of a Nyex saturated with phenol in batch and continuous ERG reactors (Hussain et al., 2013).

Often organic compounds are only partially degraded and are transformed into stable DPs. The similarity of the DPs molecular structure to that of their parent compound, often means that these DPs can have comparable biological effects and in some cases heightened toxicity and adverse effects (Parsons, 2008). Furthermore, often various DPs are formed and their synergistic effect on humans and wildlife is unknown (Ribeiro et al., 2015).

4. Aims of the Project

The overarching aim was to test and assess the performance of Nyex for the removal of several current-use pesticides, specifically to examine sorption behaviour of these chemicals and observe the effect of an electrical current on their chemical behaviour and fate. Specific objectives include the development of a reproducible analytical method using HPLC instrumentation; determining sorption isotherms using a laboratory-based Nyex testing regime, and deducing sorbed-chemical behaviour/degradation in the presence of an electrical current.

1. Analytical Method:

- Develop an optimised and robust analytical method for the identification and quantification of atrazine and pirimicarb at µg/L and ng/L levels
- Develop an analytical method for the detection of any potential DPs

2. Nyex Performance and Behaviour:

- Investigate the performance of the Nyex adsorbent material at removing atrazine and pirimicarb
- The kinetics of adsorption will be investigated to determine the minimum adsorbate - Nyex contact time required to reach equilibrium
- Using this minimum time to reach equilibrium the adsorptive performance will be assessed using adsorption isotherms and using a range of different adsorption models to assess the data
- Compound mixture adsorption isotherm experiments, conducted in raw water, will help to evaluate any preferential removal of atrazine and pirimicarb and whether there is any competitive influence on their removal due to the presence of any natural organic matter

3. Electrochemical Oxidation:

- Saturate the Nyex with atrazine and pirimicarb individually to establish that any removal of the compound from the ERG is due to the breakdown of the compound and not further adsorption onto the Nyex
- Test the performance of the Nyex during ERG to investigate its ability to remove and treat atrazine and pirimicarb at trace level concentrations when a current is applied
- Develop an understanding of the adsorbed chemicals behaviour and fate during ERG

4. Degradation Products:

- Investigate the production of any DPs during ERG of the Nyex
- Try to tentatively identify any DPs

Chapter 2 – Materials and Methods

1. Materials

1.1. Chemicals and Reagents

PESTANAL analytical standards atrazine (neat, CAS number 1912-24-9), diazinon (neat, CAS number 333-41-5), pirimicarb (neat, CAS number 23103-98-2) and simazine d_{10} (neat, CAS number 220621-39-6) were purchased from Sigma Aldrich (UK). Methanol and acetonitrile (ACN) (both HPLC grade), were purchased from Fisher Scientific. Deionised (DI) and ultrapure water (MQ) was prepared using a Millipore Milli-Q system (Millipore, Billerica, MA, USA).

1.2. Arvia Tubular Lab Unit

A picture of the Arvia tubular unit is presented in Fig. 3.

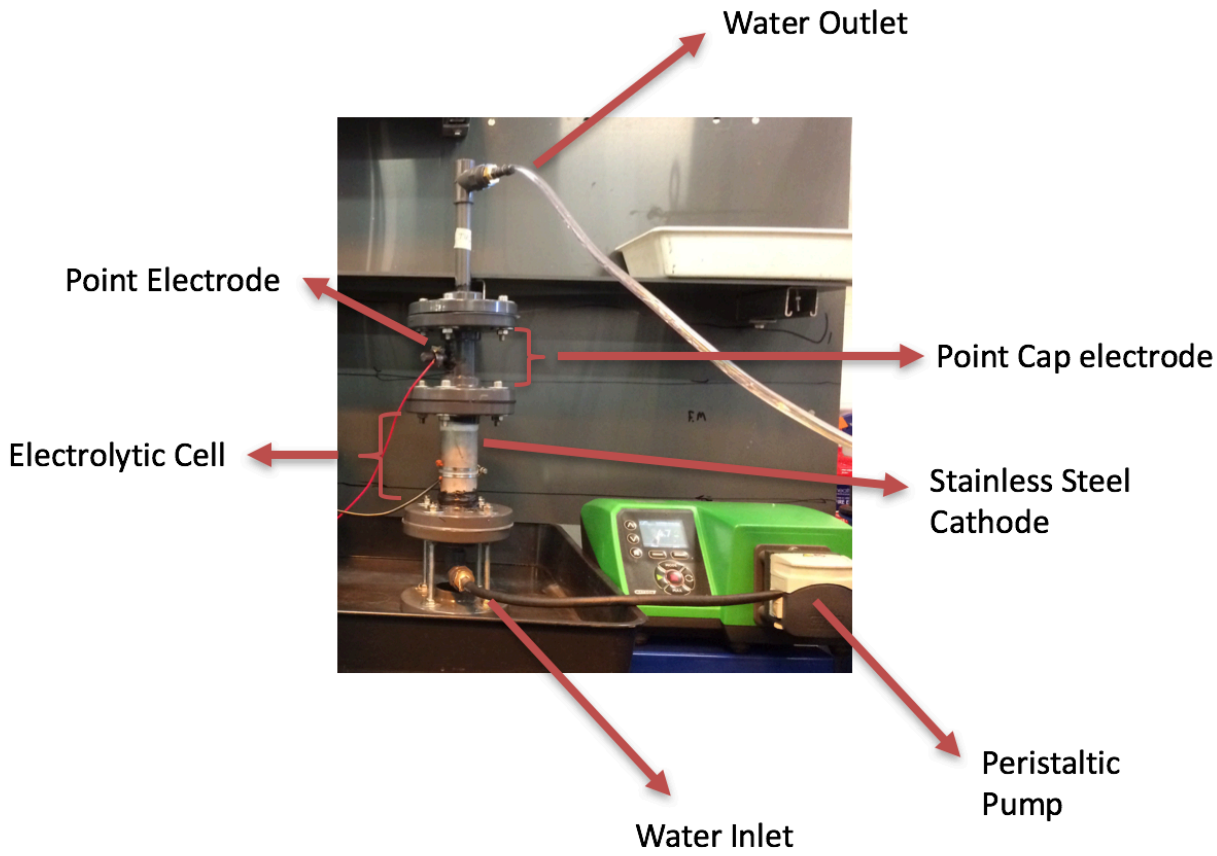


Fig. 3. Picture of the tubular unit showing an upward flow configuration

The adsorbate stock solution enters from the bottom of the unit (upward flow) with the aid of a peristaltic pump. The adsorbate solution travels through the vertical electrolytic cell, which is composed of an anodic compartment surrounded by cathodic stainless material. The anode and cathode were separated by a Daramic 350 micro-porous membrane.

The Nyex bed within the electrolytic cell was 15 cm in height and the diameter of the electrolytic cell was 4 cm. The point electrode was made of graphite and was located above the electrolytic cell in the point cap electrode (PCE) (See Fig. 4.). The Nyex bed in the PCE, which was in contact with the point electrode, acts as an electric feeder into the electrolytic cell. Thus, in the PCE, adsorption is solely taking place whereas, in the electrolytic cell the adsorbate molecules are being electrochemically oxidised.

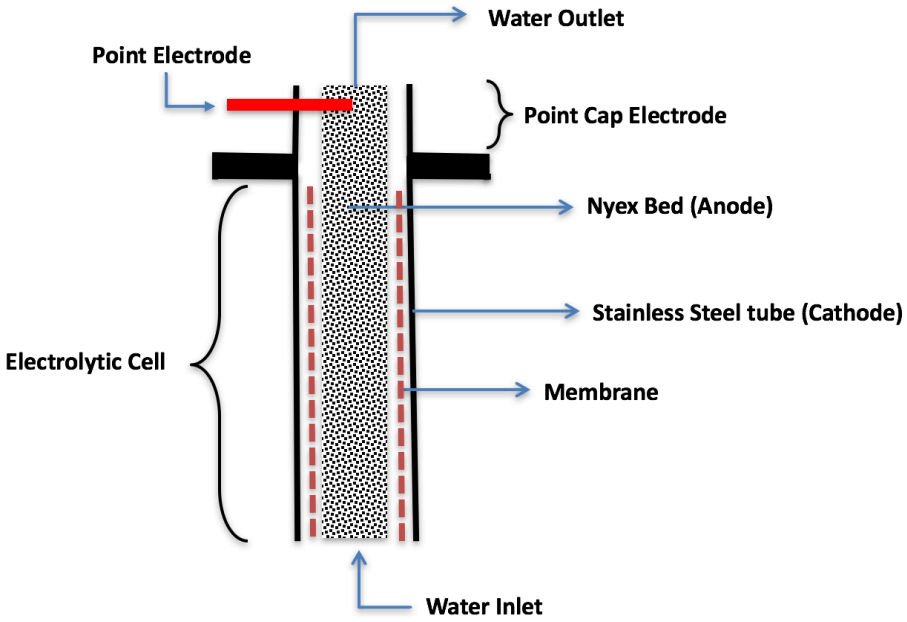


Fig. 4. Representative schematic of the tubular unit

1.3. Nyex

The Nyex 2112 is a proprietary material supplied by Arvia Technology Ltd. It is a granular graphite-based adsorbent with an average particle size of 250 – 2000 µm. The Nyex 2112 is relatively non-porous and thus the Nyex has a low adsorptive capacity for organic compounds. An SEM image of the granular Nyex (Fig. 5.) depicts its granular shape and rough surface morphology.

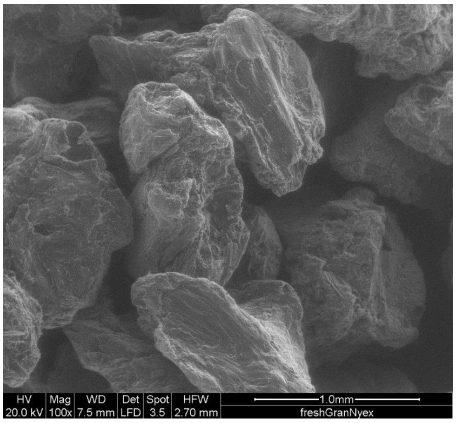


Fig. 5. SEM image of granular Nyex

Nyex 2112 is highly conducting and has been shown to have the capacity be electrochemically regenerated. Brown et al., (Brown et al., 2004a, Asghar et al., 2012, Nkrumah-Amoako et al., 2014, Nabeerasool et al., 2015) have demonstrated that a system based on anodic ERG of this graphite-based adsorbent is capable of the removal of various organic compounds from dyes to pesticides from water.

2. Methods

2.1. Experiment I – Extraction Methodology

Solid phase extraction (SPE) is a technique used for sample preparation which follows principles and concepts similar to liquid chromatography (LC) columns for the selective adsorption of target analytes from a matrix.

Like an LC column, an SPE tube contains a solid phase that is made up of unique bonds. If an analyte has no affinity for the solid phase, it will travel quickly through the SPE tube and elute. This analyte is not retained and has a low *k* value. However, if an analyte travels only marginally down the SPE tube, it is said to be retained on the SPE tube and will have a high *k* value. This results in the analyte of interest being isolated on the SPE tube. Subsequently, a solvent, in which the analyte is highly soluble is percolated through the tube, eluting the analyte of interest.

The aim of SPE tubes is:

- To remove interferences to achieve better chromatography and attain more reliable and consistent analytical results

- To concentrate samples for higher detection sensitivity and lower limits of detection
- Solvent exchange

There are a variety of SPE tubes that contain different bonded phases. These different bonded phases will provide selectivity based on the compound and its physical and chemical properties. The different retention mechanisms include: reverse phase (RP), normal phase and ion exchange. Based on the physical and chemical properties of atrazine and pirimicarb and previously reported SPE tubes used in peer reviewed papers, it was determined that a C-18 RP SPE tube would be suitable for our compounds (Pinto and Jardim, 2000, Melo et al., 2005, Carabias-Martinez et al., 2005).

Supelclean LC-18 tubes (500 mg) (Supelco, UK) were used for the SPE procedure. Before using the SPE tubes for analyte enrichment, the SPE tubes were tested for their atrazine and pirimicarb recovery rates. Spiked DI water samples containing atrazine and pirimicarb at three different concentrations were tested: 1, 0.25 and 0.05 mg/L. The extraction, at each concentration, was repeated five times. The mean value was used as the analyte recovery rate.

2.2. Experiment II – Adsorption Studies

2.2.1. Adsorption Kinetics

Individual atrazine and pirimicarb solutions (250 μg/L; 3 L), prepared in DI water, were mixed with a magnetic stirrer with 12 g of pre-washed and dried Nyex for 4 h. Samples (30 mL) were collected every 10 min for the first 60 min and thereafter every 60 min. Samples were then extracted using the SPE procedure described in section 2.6.1. and analysed by HPLC/DAD.

2.2.2. Adsorption Isotherms

i. Single Compound Experiment

Nine individual concentrations of atrazine and pirimicarb (1, 2.5, 5, 10, 25, 50, 100, 250 and 500 μg/L; 400 mL) were prepared in DI water. 200 mL of these solutions were set aside to determine the initial concentration of our compound in solution and the remaining 200 mL aliquots were mixed with 0.8 g of pre-washed and dried Nyex for 2 h. Samples were then extracted using the SPE procedure described in section 2.7.1. and analysed by HPLC/DAD.

ii. Mixed Compound Experiment

Nine concentrations of a combined atrazine and pirimicarb solution (1, 5, 10, 25, 50, 100, 250 and 500 μg/L; 400 mL) were prepared with water taken from Runcorn Canal, Runcorn, UK. The isotherm study was repeated as described in 2.2.2. i. The pH, conductivity, colour and total organic carbon (TOC) of the canal water were also measured and recorded.

The amount of each compound adsorbed (at equilibrium) per mass of adsorbent is given as q_e (μg/g) and was determined using equation (3).

3)

$$q_e = (C_0 - C_e)\, {}^{V}/_{m}$$

Where C_0 is the initial concentration of our compound in solution (μg/L), C_e is the concentration of compound remaining in solution (μg/L) at equilibrium, m is the mass of adsorbent used (g) and V is the volume of the solution (L) used in the experiment.

The adsorption data was then tested against a Langmuir adsorption isotherm model given by equations (4) and (5).

4)

$$q_e = \frac{Q_0 K C_e}{1 + K C_e}$$

Linearization gives:

5)

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left(\frac{1}{K Q_0}\right)\left(\frac{1}{C_e}\right)$$

Where Q_0 represents the maximum adsorption capacity (mono-layer coverage) (μg/g) and where $1/KQ_0$ and $1/Q_0$ are the model constants and are derivable from a best fit regression line to a plot of $1/q_e$ vs. $1/C_e$.

An alternative form of Langmuir, plotting C_e/q_e vs. C_e should give a straight line with intercept $1/KQ_0$ and slope $1/Q_0$ (equation 6).

6)

$$\frac{C_e}{q_e} = \frac{1}{KQ_0} + \frac{C_e}{Q_0}$$

The adsorption data was also fitted to a Freundlich adsorption isotherm model given by the equations (7) and (8).

7)

$$q_e = K_f C_e^{1/n}$$

Linearization gives:

8)

$$\log q_e = (1/n) log C_e + \log K_f$$

The Freundlich model parameters, *1/n* and K_f, are system specific constants that may be derived from a best fit regression line on a *log* (q_e) vs. *log* (C_e) plot.

2.3. Experiment III – Nyex Saturation

Before conducting Nyex ERG experiments, it is necessary to saturate the Nyex at or above the adsorbate feed concentration to be treated. This is important as it will act as a base-line from which the performance of the system under applied electric current can be determined. I.e.: we wish to conclusively show destruction (post adsorption) and not that the data is being masked by adsorption.

In previous studies, the Nyex was saturated by passing a known volume of solution through the Nyex bed, which sat within the unit. As these studies were investigating the treatment of highly concentrated adsorbate solutions, saturation was rapid and thus the volume of solution required was low. However, the objective of the present study was to investigate whether ERG of the Nyex could successfully treat and remove atrazine and pirimicarb at trace level concentrations. Investigating the treatment of these compounds at trace level concentrations thus presented new practical challenges.

Challenges with pre-saturating the Nyex at such a low concentrations were:

1) Saturation would require a rather large volume of water approx. 1000 L. This would enable enough amount of the MP to flow through the system such that it will be beyond the adsorptive capacity of the Nyex.
2) Time would be an issue, as at the flow rate chosen, it would take an impractically long length of time to saturate the Nyex bed
3) The availability of treatment unit

The possible methods suggested to saturate the Nyex prior to ERG were:

1) To use a large volume approx. 1000 L of adsorbate stock solution
2) Artificially pre-saturate the Nyex (i.e.: to mimic the effect of having a large volume passing through the adsorbent without current) and then start the trial with current (i.e.: ERG).

All the above challenges led to the adoption of method option 2), whereby the Nyex was artificially pre-saturated with the pesticide prior to commencing the ERG experiment. Thus, in order to establish how much atrazine and pirimicarb was required to saturate the Nyex at a low µg/L concentration, breakthrough curve (BTC) experiments at higher concentrations were conducted.

2.3.1. Breakthrough Curve

Individual compound solutions of atrazine and pirimicarb were prepared in tap water (500 µg/L) and were passed through two separate tubular prototype units at a flow rate of 2 L/h. An initial effluent sample (200 mL) was collected after the first hour and thereafter every 2 h for the first day, thereafter samples were collected every 24 h. The samples were extracted using the SPE procedure described in section 2.6.1. and analysed by HPLC/DAD. Control samples from the drum containing the stock solution were also collected to monitor any compound adherence to the surfaces of the drum.

BTCs are most commonly expressed as normalised concentrations against time. This normalised concentration is a ratio of the effluent concentration at a given time (C_t) to the influent concentration (C_0) and is expressed as C_t/C_0 (Adeyemi, 2017).

The volume (V) of effluent passed at any given time (t) can be estimated by knowing the volumetric flow rate (Q).

$$V = Qt$$

Where, *V* is measured in Litres (L), *Q* (L/h) and *t* (h)

The amount of atrazine and pirimicarb recovered, q_t, from the effluent samples could be estimated over the time taken for the bed to become "saturated". This allowed for the amount of compound adsorbed onto the Nyex to be determined. This quantity can be estimated through integrating the recovered atrazine and pirimicarb concentration (C_r) against time (t). The amount of recovered atrazine and pirimicarb is the difference between the inlet and effluent concentrations (Adeyemi, 2017):

9)

$$q_t = QA = Q\int_{t=0}^{t=t} C_r dt \ (\mu g)$$

Similarly, q_t, can be estimated from the BTC:

10)

$$q_t = QA = Q\int_{t=0}^{t=t} \left(1 - \frac{C}{C_0}\right) dt \ (\mu g)$$

Using the approximate numerical equation of the trapezium rule, the integral aspect of equation (10) can be determined using the BTC data. "A" is an integral function which describes the area of the BTC as shown in Fig. 13, page: 59 (Adeyemi, 2017).

2.3.2. Artificial Pre-saturation

A 0.75 mg/L atrazine compound solution, prepared in tap water, (4 L; 3 mg of atrazine) was mixed for 18 h with 166 g of pre-washed and dried Nyex. This pre-saturated Nyex was then transferred into the tubular unit (see Fig. 3.). Initially a 10 µg/L atrazine solution was passed through the Nyex in the tubular unit for 20 h (1 L/h), followed by a 3 µg/L atrazine solution (1 L/h). It was established that the Nyex was saturated at 3 µg/L when the effluent sample concentrations were 3 µg/L. The samples were analysed by HPLC/MS.

A 1 mg/L pirimicarb compound solution, prepared in tap water, (4 L; 4 mg of pirimicarb) was mixed for 18 h with 166 g of pre-washed and dried Nyex. Again, this pre-saturated Nyex was subsequently transferred into the tubular unit. Initially a 10 µg/L pirimicarb solution was passed through the Nyex in the tubular unit for 20 h (1 L/h), followed by a 1 µg/L pirimicarb solution (1 L/h). It was established that the Nyex was roughly saturated at 1 µg/L when the effluent sample concentrations were almost 1 µg/L. The samples were analysed by HPLC/MS.

For both atrazine and pirimicarb, samples from the drum containing the stock solution were also collected to monitor any compound adherence to the surfaces of the drum.

2.4. Experiment IV – Electrochemical Regeneration

Once it was established that the Nyex was saturated with atrazine and pirimicarb in the two separate tubular units, a current of 0.125 A (current density of 0.66 mA/cm^2) was continuously applied. A 3 µg/L atrazine solution and 0.7 and 0.9 µg/L pirimicarb solutions were passed through the corresponding units at a flow rate of 1 L/h, while the current was applied. Effluent samples were collected every hour on the first day and thereafter twice a day. The samples were analysed by HPLC/MS.

2.5. Experiment V – Degradation Product Formation

The effluent samples, collected from the ERG experiments, were used to tentatively identify the formation of any DPs. Full-scan mode on the mass spectrometer (MS) produced a spectrum allowing for the identification of any new ions. The analysis is described in more detail in section 2.6.4 and in the appendices section 2.3.

2.6. Analytical Methods

2.6.1. Sample Preparation

In this study, direct analysis of samples on the HPLC/DAD could not be performed. A sample preparation step had to be included in the analytical method to concentrate the analytes in the samples as their concentrations were below the limit of detection of the HPLC/DAD. This step also helped to remove any major analyte interferences and provided a method for sample solvent

exchange from water into ACN.

Analyte enrichment and purification was achieved using SPE tubes (Supelclean LC-18 tubes (500 mg), Supelco, UK). The SPE procedure was as follows: The Supelclean LC-18 tubes were conditioned with 6 mL ACN, then 6 mL MeOH, followed by 3 mL DI water. The water sample to be extracted was then percolated through the tube with the assistance of a vacuum manifold (Supelco Visiprep SPE Vacuum Manifold) at a rate of 4 mL/min. After the sample was passed through the tube, the tubes were dried under full vacuum for 20 min to remove residual water and the analytes were eluted into a test tube by use of 3 mL ACN. Under a flow of nitrogen gas (N_2), the eluate was evaporated to dryness and the sample was resolubilised using mobile phase B (ACN). The sample containing the analytes was stored at 4 ± 2 °C until use.

2.6.2. Calibration Standards

To quantify unknown concentrations of analytes in a sample, a set of calibration standards (CS) were prepared. These CSs contain a range of known concentrations of the analytes of interest. To improve the robustness of the method an internal standard (IS), at a fixed concentration, was added. The analyte/IS response ratio was used to create a calibration line by plotting it against the analyte concentration. This function was used to quantify the quality control (QC) standards and unknown samples. Additionally, all standards and samples were prepared in a solvent composition as similar as possible to the mobile phase composition at the beginning of the HPLC run to ensure good chromatographic performance and peak shape.

In this study, both individual atrazine and pirimicarb CSs and calibration mixture consisting of atrazine and pirimicarb, at a range of concentrations, were prepared for the identification of the two pesticides on the HPLC/DAD. The final concentrations of the pesticide standards were 1, 2.5, 5, 10, 25, 50, 100 and 150 mg/L.

For pesticide identification and quantification on the LC/MS calibration mixtures consisting of atrazine and pirimicarb at a range of concentrations, along with an IS (simazine d_{10}), at a single concentration of 20 µg/L, were prepared. The final concentrations of the pesticide standards were 0.01, 0.1, 1, 2.5, 5, 10, 25, 50 and 100 µg/L.

2.6.3. HPLC/DAD and LC/MS

HPLC/DAD (Agilent Technologies 1220 Infinity LC) with diode array detection (DAD) at wavelengths of 220 nm and 250 nm was used to resolve and quantify atrazine and pirimicarb, respectively. A Kinetex EVO C18 EVO 4.6 x 150 mm 5-micron LC column was used for separating the analytes and was maintained at 30 °C. Solvent A consisted of MQ water and solvent B consisted of ACN. Gradient elution with the following profile was used. Initial solvent ratio (solvent A:solvent B) was 70:30 (v/v). This was followed by a linear increase of solvent B to 45 % from 0 to 7 min. From 7 to 9 min the initial solvent ratio was re-established allowing the system to re-equilibrate prior to subsequent sample injection. The total run time was 9 min at a constant flow rate of 1 mL/min. Analytes were monitored using a DAD detector. Representative chromatograms showing the RTs of the pesticide analytes are presented in the appendices section 1. (Fig. 26 and Fig. 27.).

LC/MS (Agilent Technologies 1100 Series HPLC system coupled to a Hewlett Packard MSD) was used to resolve and quantify atrazine and pirimicarb as well as any of their DPs. An Agilent Poroshell 120 EC-C18 2.1 x 100 mm 2.7-micron LC column was used for separating the analytes and was maintained at 30 °C. Solvent A consisted of MQ water and solvent B consisted of ACN. Gradient elution with the following profile was used. Initial solvent ratio (solvent A:solvent B) was 70:30 (v/v). This was followed by a linear increase of solvent B to 45 % from 0 to 6 min followed by a rapid increase of solvent B to 90 % from 6 to 7 min. This solvent ratio was maintained from 7 to 8 min. Then from 8 to 9 min the initial solvent ratio was re-established and the system could re-equilibrate for 7 min. The total run time was 16 min at a constant flow rate of 0.2 mL/min.

Analytes were monitored using single ion monitoring (SIM) in positive ionization mode. Quantification ion mass-to-charge ratio (*m/z*) for atrazine, diazinon, pirimicarb, simazine (d_{10}) are shown in Table 2. A dwell time of 138 msec was used for all ions.

Table 2. HPLC/MS quantification and confirmation ions and corresponding fragmentor voltages of the target ions.

Compound	Quantification ion (QI) *m/z*	Confirmation ion (CI) *m/z*	Fragmentor Voltage (V)
Atrazine	216.1	218.1	90
Diazinon	305.1	169.1	130 (QI), 180 (CI)
Pirimicarb	239.1	182.1	90 (QI), 150 (CI)
Simazine (d_{10})	212.1	214.1	60

The mass spectrometric parameters were as follows: N_2 was used as the drying gas at a flow rate of 11 L/min and a temperature of 350 °C. The nebulizer pressure (psi) was 45 and the capillary voltage was 4500 V. Details on the HPLC/MS method optimisation are discussed in the appendices section 2. with representative chromatograms showing the *m/z* values and RTs of the pesticide analytes.

2.6.4. Degradation Products

LC/MS was used for the tentative identification of the formation of any DPs. The same mobile phase gradient used for the identification and quantification of atrazine and pirimicarb in SIM mode was used for identification of the DPs in full-scan mode. The *m/z* range chosen for the DPs was 70 – 250 and a default value of 90 was chosen for the fragmentor voltage. Representative chromatograms showing the *m/z* values and RTs of the pesticide DP analytes are presented in the appendices section 3.

2.6.5. Quality Controls

QCs must be used to support any study in which analytical methods are used. They help to establish and validate that the optimised method is fit-for-purpose.

In this study, several QC methods were used:

i. Intra- Sequence QC Sample

QC samples are added to each sequence to provide sequence-level QC and demonstrate the repeatability, accuracy, precision and stability of the method. To achieve this the QC sample must reach a predefined level of accuracy for the sequence to be regarded as acceptable. The QC samples contain a known amount of analyte and represent the matrix of the samples being analysed. If the method performs in an acceptable manner, as determined by the QC samples, then the results of the samples containing unknown concentrations of analyte can be reported with confidence.

ii. Internal Standard

Since a MS detector separates analytes by their *m/z* ratio, labelled IS, that can usually not be separated by the LC, will be separated by their difference in mass to the corresponding unlabelled analyte. These labelled ISs are frequently spiked into samples, CSs and QCs. By dividing the analyte peak area (APA) by the IS peak area (IPA) (APA/IPA) the APA is normalised. This normalisation can help achieve reliable quantitative analysis by controlling instrumental variability by correcting effects such as fluctuations in the sample injection volume and sensitivity of the detector. The IS can also help monitor any matrix effects i.e.: ion suppression.

iii. Intra-day QC samples

The intra-day precision and accuracy was tested by injecting a known standard (1 µg/L) ten times twice in one day. This was done in two batches, once in the morning and once in the evening. This gave an insight into the precision and short term variability of the instrument.

Chapter 3 – Results and Discussion

1. Experiment I – Extraction Methodology

For the adsorption studies and the artificial pre-saturation of the Nyex (Experiment II and III), samples were pre-concentrated using a SPE protocol. Atrazine and pirimicarb recoveries were determined prior to sample analysis using Supelclean LC-18 tubes (500 mg) connected to a SPE manifold and vacuum pump. Subsequently, the solution was analysed by HPLC/DAD. The details of the SPE protocol used are shown in Table 3. While, the recoveries and relative standard deviation values resulting from this SPE protocol are listed in Table 4.

Table 3. Conditions used in the SPE protocol

Starting Concentration (mg/L)	Extraction Volume (mL)	Elution Volume (mL)	Final Concentration (mg/L)
1.0	20	3	6.7
0.25	90	3	7.5
0.05	480	3	8.0

Table 4. Recovery and relative standard deviation of atrazine and pirimicarb

Starting Concentration (mg/L)	Number of repeats per compound	Average Recovery (%)	
		Atrazine	Pirimicarb
1.0	5	127 ± 4	103 ± 9
0.25	5	113 ± 12	109 ± 12
0.05	5	113 ± 13	120 ± 2

The recovery and relative standard deviation values indicate that the Supelclean LC-18 SPE tubes can effectively retain both atrazine and pirimicarb. Thus, it is possible to concentrate the target analyte in samples making it possible to work at much lower concentrations, while having confidence in the experimental data.

2. Experiment II – Adsorption Studies

2.1. Adsorption Kinetics

Adsorption kinetic experiments (AKEs), using atrazine and pirimicarb, were done to establish the minimum Nyex contact time required to achieve equilibrium. From these experiments, a mixing time of 120 min was determined to be sufficient for the adsorbent to attain equilibrium conditions. From a starting concentration of 250 µg/L, on average in two hours, the Nyex removed 25 µg of atrazine per gram of Nyex (25 µg/g). Similarly for pirimicarb, at a starting concentration of 250 µg/L, on average in 120 min, the Nyex removed 36 µg per gram of Nyex (36 µg/g). These results indicate that there is a greater affinity for the adsorption of pirimicarb onto the Nyex over atrazine. Adsorption of atrazine and pirimicarb was determined to be fast with 70 % and 72 % of the equilibrium concentration reached within 30 min for atrazine and pirimicarb, respectively (Fig. 6. and 7.).

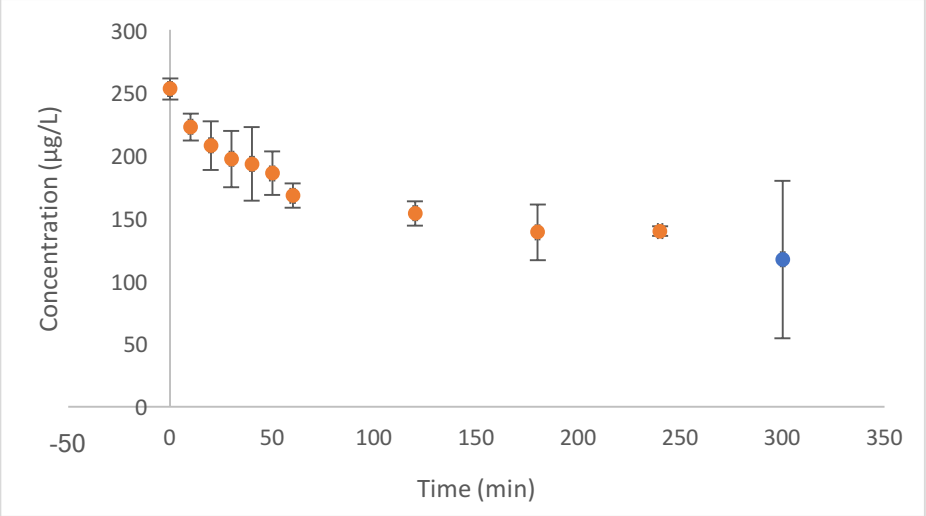


Fig. 6. Adsorption kinetics of atrazine onto Nyex performed under batch conditions using 0.8 g of Nyex and 200 mL atrazine solution with an initial concentration of 250 µg/L. In this figure, the error bars represent error to one standard deviation. The point at 300 min has been excluded in the formation of the trend line. There was a lot of variability in this point and the standard deviation was high.

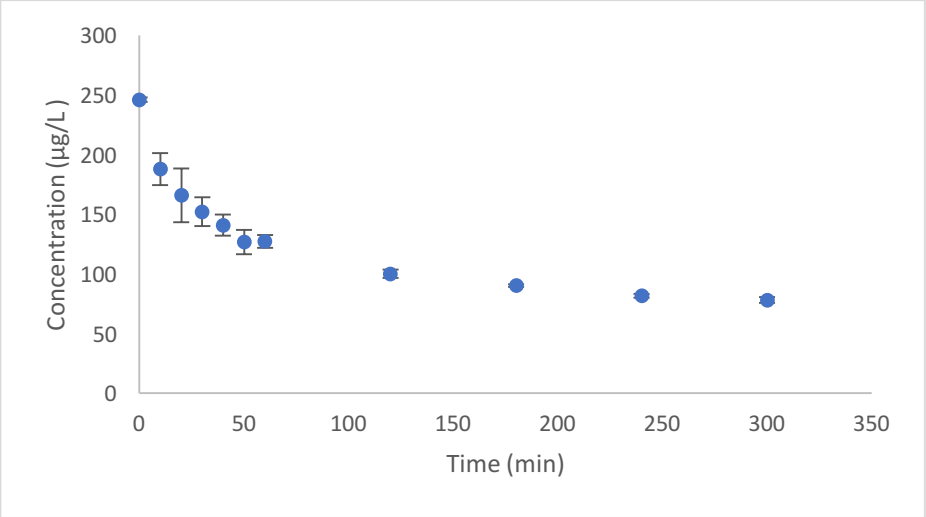


Fig. 7. Adsorption kinetics of pirimicarb onto the Nyex performed under batch conditions using 0.8 g of Nyex and 200 mL pirimicarb solution with an initial concentration of 250 µg/L. In this figure, the error bars represent error to one standard deviation.

The initial slope of the curve for atrazine and pirimicarb, from 0 – 50 min, is the steepest part of the curve. This indicates that the external solution concentration decreases quickly. The slope of the curve begins to level off as the rate of the decrease of the external solution concentration is starting to slow down, and is followed by a plateau. These characteristics of the curve provide some early information about the adsorption process occurring. The initial steep slope illustrates the high availability of adsorption sites on the Nyex. It also shows that there is an affinity for the adsorption of atrazine and pirimicarb over competing water molecules. As site availability decreases there is a corresponding decrease in the uptake rate of adsorbate molecules onto the Nyex. This is demonstrated by the gradual levelling off of the curve. Then once there is no more attraction for any more adsorbate molecules on the adsorbent, the curve will plateau. This is significant as this demonstrates that equilibrium has been achieved. This means that there is a balance between the solute molecules in the external solution and what is adsorbed onto the adsorbent. Additional adsorption can only occur by raising the external solution concentration.

For both atrazine (Fig. 6.) and pirimicarb (Fig. 7.) pseudo-equilibrium was reached at 120 min. Regarding atrazine, the error bar of the data point at 300 min is quite large. This indicates that there was some additional adsorption in one of the triplicates and de-sorption in another. Additional adsorption could occur as the solution volume to Nyex ratio is decreasing (30 mL removed for every sample) leading to increased adsorption. Another consideration is that the magnetic stirrer could be creating smaller Nyex particles/fines, creating new adsorption sites and adsorbing more of the

compound. The increase in concentration could be due to de-sorption of the compound due to the high velocity of the magnetic stirrer.

Atrazine AKEs were conducted by Brown et al., (2004a) using a very early generation of Nyex, the Nyex 100. Nyex 100 is a wet powder containing non-porous particles with no internal surface area. In a 5 mg/L atrazine solution, equilibrium was reached within 60 min with 80 % of the equilibrium value being achieved within 10 min. In comparison to the present study, the rate of adsorption was significantly faster and the contact time required to reach equilibrium was considerably lower. This can be explained by the higher atrazine solution concentration used in this study (5 mg/L vs. 0.25 mg/L). Significantly more adsorbate molecules are present in the solution surrounding the Nyex, leading to quick adsorption and a lower equilibrium time. This effect was demonstrated by Nabeerasool et al., (2015) who conducted AKEs, at a wide range of initial concentrations, for the adsorption of metaldehyde onto Nyex 1102. Three initial concentrations were used, namely: 0.25, 2 and 12 mg/L. For 2 and 12 mg/L, equilibrium was reached in 20 min whereas, in the case of the lowest initial concentration, 0.25 mg/L, equilibrium was not reached until 50 min. This highlights how the rate of adsorption onto the Nyex can be influenced by lower concentrations and thus affect the equilibrium time.

Although it has been demonstrated that lower contaminant concentrations are adsorbed more slowly onto the Nyex, in contrast to AC these determined equilibrium times are much faster. Adsorption onto AC, either in its granular (GAC) or powdered form (PAC), is a very popular technique used to treat water contaminated with dissolved organic contaminants (Brown et al., 2004a). Its popularity is due to its high adsorption capacities for these dissolved organic contaminants. This is as a result of its micro-porous structure, leading to its high internal surface area. AC has contrasting characteristics to the adsorbent used in this study. Nyex has markedly less total surface area (TSA) (roughly 1 m^2/g) in comparison to AC (which has a surface area of 600 – 1200 m^2/g) (Nkrumah-Amoako et al., 2014).
The influence the surface area has on the adsorption of atrazine is demonstrated by (Baup et al., 2000). In this study the initial concentration of the atrazine solution was 0.25 mg/L and equilibrium was reached after 2 to 3 days. For AC, as a result of its high TSA, intra-particle diffusion is a rate limiting step and is responsible for these long equilibrium times. Since the Nyex has a low TSA, intra-particle diffusion is negligible (and irrelevant) and is one of the major advantages of the Nyex over AC.

2.2. Adsorption Isotherms

The most basic adsorption isotherm is constructed by plotting the solid-phase concentration (q_e) against the liquid-phase concentration (C_e), at equilibrium. The corresponding graph illustrates the relationship and equilibrium behaviour of the adsorbate molecules between these two phases.

Fig. 8. demonstrates that there is a clear relationship between the adsorbate concentration in the liquid phase and adsorbate concentration accumulated on the solid phase. However, in comparison to atrazine, the initial slope of the curve for pirimicarb is steep. This steep slope is not maintained as it does begin to decrease with increasing liquid phase concentration. Further from the origin, the slope of the curve for atrazine, begins to decrease. It is clear that higher liquid phase concentrations have a lesser effect on the adsorption of atrazine onto the Nyex, in comparison to pirimicarb. This highlights that the Nyex has a greater adsorption capacity for pirimicarb. More pirimicarb adsorbate molecules are adsorbed onto the solid phase (q_e) and thus, the corresponding C_e value is lower in comparison to that for atrazine.

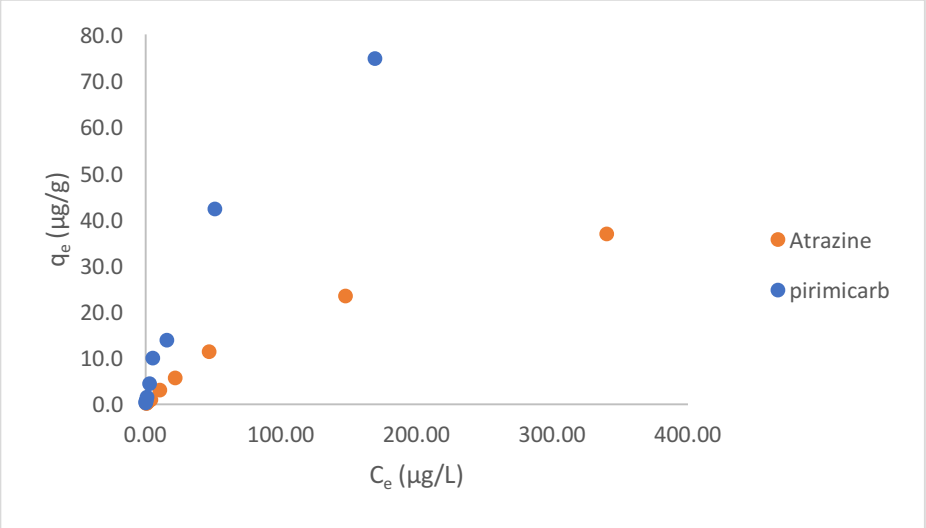


Fig. 8. Atrazine and Pirimicarb adsorption isotherm of the solid-phase concentration (q_e) versus liquid-phase concentration (C_e) at equilibrium

The shape of the isotherms obtained are indicative of the adsorption process occurring. As previously described in chapter 1 (section 4.2.) Giles et al., (1960) developed a system for the classification of adsorption isotherms depending on the initial and upper slopes of the curve. This system divides all isotherms into four main classes: L-shaped curves, S-shaped curves, H-shaped curves and C-shaped curves. The slope of the initial curve is dependent on the rate of change in binding site availability, due to the increase of adsorbate molecules being adsorbed.

In the case of atrazine, molecules are being adsorbed onto the Nyex however, with the increase in liquid phase concentration more binding sites on the Nyex are filled. This makes it increasingly difficult for adsorption to continue at the same rate. Thus, as less adsorption is occurring, this leads to the decrease in the slope of the curve, which correspondingly results in higher liquid-phase concentrations.

The fact that the slope of the curve for pirimicarb is steeper in comparison to atrazine is significant. This illustrates that there is a higher distribution of pirimicarb molecules, at equilibrium, adsorbed onto the Nyex. This further supports and confirms the findings in the AKEs, which also indicated a greater adsorption affinity toward the adsorption of pirimicarb. Although the initial slope of pirimicarb is steeper in comparison to atrazine, the same mechanism of adsorption is occurring. Similarly to atrazine, the shape of the pirimicarb adsorption isotherm illustrates an initial high uptake of adsorbate molecules. However, with increasing liquid phase concentration the rate at which new molecules are adsorbed, as site availability becomes more limited, decreases.

Based on the shape of the curves for atrazine and pirimicarb (Fig. 8.), the L-shaped isotherm best describes the adsorption mechanism occurring. This is one the most common isotherms obtained from crop protection products (Ecetoc). The classification system developed by Giles et al., (1960), sub-divides the four main groups, including L-shaped isotherms. These sub-divisions are characterised by the formation of extended plateau's (e.g.: L-2) and re-established enhancement of adsorption, following an initial plateau (e.g.: L-3 and L-4). In regards to both atrazine and pirimicarb it is not possible to conclusively determine whether the liquid phase concentration has ceased influencing the adsorption of adsorbate molecules onto the Nyex i.e.: the curve has not reached an extended plateau (L-2). In order to further classify and evaluate the adsorptive behaviour of atrazine and pirimicarb, a wider and higher range of concentrations would be needed. However, the objective of the present study, was to understand the adsorption mechanisms occurring at low µg/L concentrations. Thus, the corresponding concentration range investigated was low (1 – 500 µg/L).

Previous studies investigated the adsorption mechanism of phenol, benzoquinone, hydroquinone and catechol on the Nyex 1000 (Hussain et al., 2013). Like atrazine and pirimicarb, the adsorption isotherms for these aromatic compounds were reported to be best described by L-shaped isotherms.

2.2.1. Adsorption Isotherm Models

i. Single Compound Isotherms

Values of Langmuir constants Q_0 and K, Freundlich constants K_f and $1/n$, and the regression co-efficient (R^2) for atrazine and pirimicarb are listed in Table 5.

Table 5. Derived Langmuir and Freundlich adsorption isotherm parameters of atrazine and pirimicarb from the single compound experiment

Pesticide	Langmuir isotherm $1/C_e$ vs. $1/q_e$			Langmuir isotherm C_e vs. C_e/q_e			Freundlich isotherm Log C_e vs. Log q_e		
	R^2	Q_0	K	R^2	Q_0	K	R^2	1/n	K_f
Atrazine	0.990	11.2	0.019	0.887	68.0	0.004	0.957	0.83	0.356
Pirimicarb	0.996	36.5	0.037	0.938	106.4	0.013	0.982	0.85	1.375

Where the units for Q_0 are µg/g, K are L/µg and K_f are L/g

For both atrazine and pirimicarb, the adsorption data fits the first Langmuir isotherm model (*$1/C_e$ vs. $1/q_e$*) with a very good linear correlation (R^2 = 0.990 and 0.996) (Table 5. and Fig. 9.). The derived Langmuir equilibrium constant, K, is higher for pirimicarb than atrazine (0.037 vs. 0.019 L/µg) and indicates that pirimicarb has a greater affinity to be adsorbed onto the Nyex. However, the derived maximum adsorption capacity values, Q_0, of 11.2 and 36.5 µg/g, for atrazine and pirimicarb respectively, are below their highest q_e value of 36.9 and 74.8 µg/g, respectively, which corresponds to the highest concentration used in the adsorption study (500 µg/L; Fig. 8). As Q_0 is the value that represents the maximum loading capacity of the compound onto the Nyex, this indicates that, despite the high R^2 values, the model doesn't accurately represent the data.

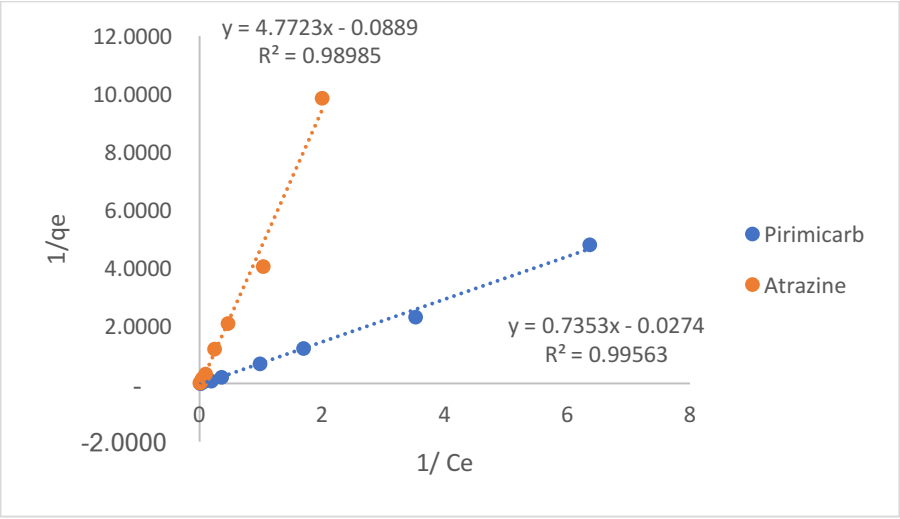


Fig. 9. Langmuir plot (*$1/C_e$ vs. $1/q_e$*) for the atrazine/Nyex and pirimicarb/Nyex system, where q_e and C_e are in µg/g and µg/L, respectively

Additionally, the data was fitted to a second version of Langmuir (C_e *vs.* C_e/q_e) (Fig. 10.). The derived Q_0 value was higher for both atrazine and pirimicarb (68.0 and 106.4 µg/g, respectively; Table 5.) than in the first version of Langmuir. These values are consistent with the corresponding q_e values (Fig. 8.). Similarly, *K* values of 0.004 and 0.013 L/µg, for atrazine and pirimicarb respectively, indicate a higher affinity for pirimicarb adsorption onto the Nyex over atrazine. For pirimicarb, the data fit very well to the second Langmuir isotherm model (Fig. 10.), where R^2 = 0.938. However, in contrast, atrazine did not fit this model as well, where R^2 = 0.887. Fitting the atrazine data to this model highlights some data point scatter at the lower solution concentrations used.

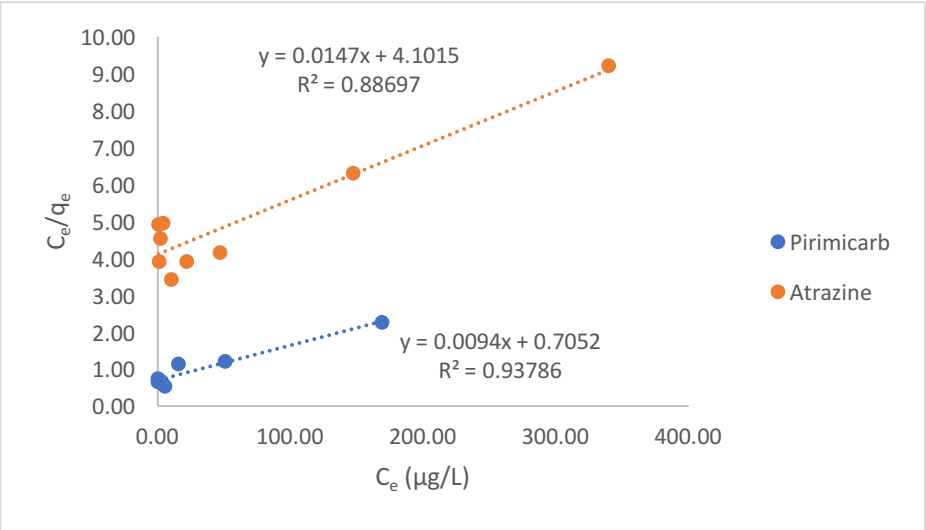


Fig. 10. Atrazine and pirimicarb Langmuir plot of C_e *vs.* C_e/q_e where q_e is in µg/g

Finally, the atrazine and pirimicarb data was fitted to the Freundlich isotherm model (Fig. 11.). For both atrazine and pirimicarb, the data fit with a high linear correlation (R^2 = 0.957 and 0.982, respectively) (Table 5.).

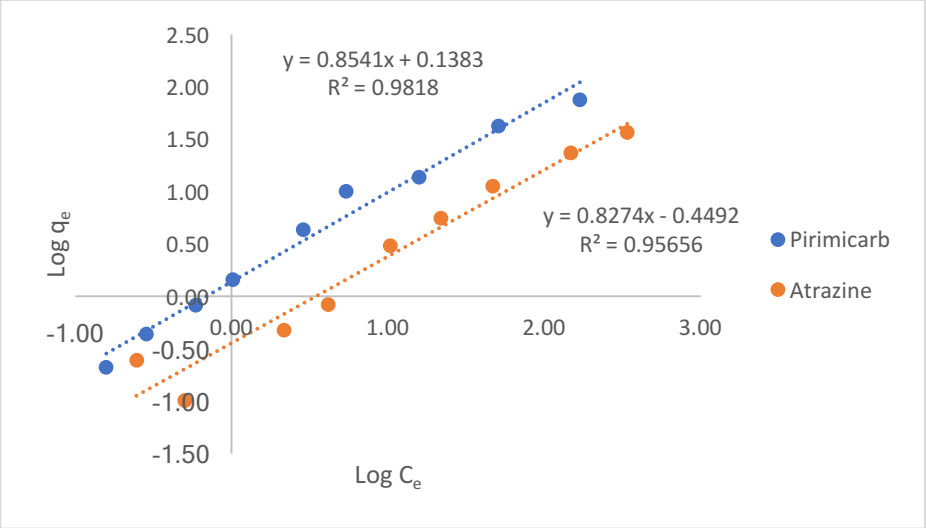


Fig. 11. Atrazine and pirimicarb Freundlich log-log plot of solid-phase concentration (q_e) versus liquid-phase concentration (C_e) at equilibrium

1/n is a measure of the adsorption intensity and this exponent describes the linearity of adsorption over a concentration range. It is most common that *1/n* values range from 1 downwards. A value of 1 would mean that there is no degree of curvature of the isotherm curve, as the relative adsorption of the adsorbate molecules was the same over the whole concentration range tested (i.e.: C-shaped isotherm) (Ecetoc). Typically, *1/n* values will range from 0.7 to 1.0. Values in this range indicate that with increasing adsorbate concentration, adsorption sites will become occupied leading to less adsorption (L-shaped isotherm). Additionally, *1/n* values < 0.7 describe a highly convex curved isotherms and *1/n* values > 1 produce a concave curve. A *1/n* value >1 indicates that adsorption increases with increasing concentration (i.e.: S-shaped isotherms). The higher the *1/n* value the more favourable the adsorption (Hussain, 2012). In the present study, the values for *1/n* were 0.83 and 0.85 for atrazine and pirimicarb, respectively. These values fall within the 0.7 to 1.0 range and are indicative of the process occurring in an L-shaped isotherm. Furthermore, this describes that adsorption is favourable for both compounds.

The Freundlich adsorption coefficient, K_f, is a parameter that provides an indication of the adsorption capacity of the adsorbent. The greater the K_f, value the higher the adsorptive capacity that molecule has for that particular adsorbent. For atrazine and pirimicarb, the K_f values were 0.356 and 1.375 L/g, respectively and indicates that the Nyex has a greater adsorption capacity for pirimicarb over atrazine. These results are consistent with the results from the AKEs (Fig. 6 and Fig. 7) and the adsorption isotherm (Fig. 8.).

These models depict the relationship and distribution of adsorbate molecules between their

concentration in the liquid phase versus their concentration on the surface of the adsorbent. These models are defined and characterised by a set of assumptions, which are linked to: i) the surface homogeneity/ heterogeneity (binding sites energies) and ii) the likelihood of inter adsorbate molecular interactions (Asghar, 2011). The Langmuir model assumptions include: surface uniformity i.e.: all binding site energies are similar, that there is mono-layer adsorption, that there is no interaction among the adsorbed molecules (Asghar, 2011, Hussain, 2012). Highly porous materials, such as AC, most often show a preference towards Langmuir-type adsorption, where monomolecular adsorption occurs as there is a large surface area and many adsorption sites (Czepirski et al., 2000). However, the Freundlich adsorption isotherm is best suited to adsorbents with rough heterogeneous surfaces as these adsorbents have multiple site types, with a range of adsorption energies available for adsorption. Furthermore, in the Langmuir model, it is assumed that at a maximum coverage, there is only a mono-molecular layer on the surface. This means that there is no stacking of adsorbed molecules. The Freundlich isotherm does not have this restriction (Ecetoc).

Thus, taking into account:

- The good R^2 values for both atrazine and pirimicarb when modelled against the Freundlich adsorption isotherm
- That the empirically derived Freundlich parameters, K_f and *1/n*, indicate that adsorption is favourable
- That the Nyex is characterised by its low surface area, non-porosity and heterogeneous binding sites, which are all favoured by Freundlich-type adsorption
- That Langmuir assumes homogeneous surface binding energies
- The inconsistencies and discrepancies from modelling the data to the two Langmuir models, in regard to their Q_0 values

All these points indicate that Langmuir-type adsorption is unlikely to occur when the Nyex is used as the adsorbent for these two compounds. Therefore, the data is best represented by the Freundlich isotherm model. This indicates that either mono- or multi-layer adsorption can occur on the surface of the Nyex. Importantly, these isotherms demonstrate that atrazine and pirimicarb are both capable of being adsorbed onto the Nyex despite its non-porosity and could therefore possibly be removed using a combined adsorption and electrochemical process.

Similar adsorption isotherm studies have been done using the Nyex by modelling the data onto either Langmuir or Freundlich adsorption isotherms. Likewise, many of these studies have shown that the data best fit the Freundlich adsorption isotherm model. This was the case in a study conducted by

Hussain et al., (2013) where, the adsorption of benzoquinone and hydroquinone onto the Nyex 1000 was best represented by a Freundlich adsorption isotherm model. Additionally, atrazine adsorption isotherm studies, conducted on the Nyex 100, determined that the data was also best represented by the Freundlich model (Brown et al., 2004a). In this study, they report the following derived Freundlich parameters: K_f = 0.279 L/g and *1/n* = 0.55. In comparison, the Freundlich parameters obtained in the present study (K_f = 0.365 L/g and *1/n* = 0.83), these parameters indicate that the Nyex 2112 has a greater loading capacity and affinity for atrazine (higher K_f value) and that the adsorption intensity is greater onto the Nyex (higher *1/n* value).

Currently, AC is one of the most widely used adsorbent for the removal of organic contaminants. This is due to its high adsorption capacity for organic compounds. The performance of AC is largely due to its porosity, which provides AC with a large surface area to accommodate different types and sizes of organic compounds. For example, in a study conducted by Lupul et al., (2015), the adsorption capacity of atrazine onto AC was reported to be 263 mg/g. This demonstrates that the adsorption capacity of AC is far greater than Nyex, where reported adsorptive capacities are in the low µg/g range (Nabeerasool et al., 2015).

ii. Mixed Compound Adsorption Isotherms

The single compound adsorption isotherm experiments allowed for the maximum performance of the Nyex to be evaluated regarding the removal of atrazine and pirimicarb. However, doing mixed compound isotherms will help assess the preferential adsorption of atrazine and pirimicarb when both compounds are present in solution and competing for the same binding sites. Furthermore, in a real-life scenario, to establish how effectively the Nyex can remove MPs from surface water, the effect of natural organic matter (NOM), should be considered. Therefore, these mixed compound adsorption isotherms were done in raw water (Canal water from Runcorn, Cheshire, UK) and the TOC content was determined to be 10.2 mg/L (Table 6.). Other properties of the water collected from Runcorn Canal are shown in Table 6. Thus, these isotherms will investigate whether the presence of NOM and two other adsorbate species (atrazine and pirimicarb) will have an effect on their adsorption onto the Nyex.

Table 6. Runcorn Canal water properties

pH	Conductivity	Colour	Total Organic Carbon
8	749 µS/cm	Yellow hue	10.2 mg/L

The preferential adsorption of atrazine and pirimicarb, in the presence of NOM, onto the Nyex was determined first (Fig. 12.). This adsorption isotherm illustrated that, at equilibrium, there is a higher distribution of pirimicarb adsorbate molecules on the Nyex rather than in the liquid phase, in comparison to atrazine. This demonstrates that when both compounds are in solution together, that there is a preference for pirimicarb adsorption onto the Nyex.

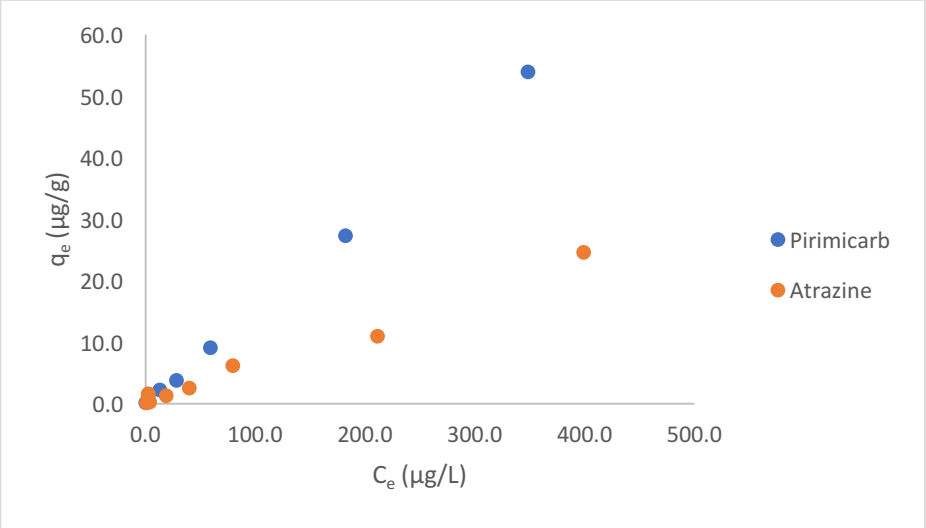


Fig. 12. Atrazine and Pirimicarb adsorption isotherm of the solid-phase concentration (q_e) versus liquid-phase concentration (C_e) at equilibrium

Using the experimental data, the adsorptive performance of the Nyex in raw water was then assessed by using a range of different adsorption models. Values of Langmuir constants Q_0 and K, Freundlich constants K_f and $1/n$, as well as the regression coefficients (R^2) for atrazine and pirimicarb are listed in Table 7.

Table 7. Derived Langmuir and Freundlich adsorption isotherm parameters of atrazine and pirimicarb from the mixed compound experiment

Pesticide	**Langmuir isotherm** $1/C_e$ vs. $1/q_e$			**Langmuir isotherm** C_e vs. C_e/q_e			**Freundlich isotherm** Log C_e vs. Log q_e		
	R^2	Q_0	K	R^2	Q_0	K	R^2	1/n	K_f
Atrazine	0.870	3.0	0.068	0.264	45.9	0.001	0.881	0.75	0.209
Pirimicarb	0.917	3.1	0.197	0.132	147.1	0.02	0.953	0.80	0.365

Where the units for Q_0 are µg/g, K are L/µg and K_f are L/g

For both atrazine and pirimicarb, the experimental adsorption data fits to the first Langmuir isotherm

model ($1/C_e$ *vs.* $1/q_e$) with a good linear correlation (R^2 = 0.870 and 0.917) (Table 7.). The derived Langmuir equilibrium constant, *K*, is higher for pirimicarb than atrazine (0.068 vs. 0.197 L/µg) and indicates that pirimicarb has a preference to be adsorbed onto the Nyex. However, similarly to the single compound isotherms, Q_0 values of 3.0 and 3.1 µg/g, for atrazine and pirimicarb respectively, are below their highest q_e value of 24.6 and 53.9 µg/g (Fig. 12). Again, this indicates that the model doesn't accurately represent the data for the mixed compound adsorption isotherm. The data was fitted to a second version of Langmuir (*Ce vs.* Ce/q_e) (Table 7.) and the derived Q_0 value was higher for both atrazine and pirimicarb (45.9 and 147.1 µg/g, respectively) than in the first version of Langmuir. These values are consistent with the corresponding q_e values. Similarly, *K* values of 0.001 and 0.02 L/µg, for atrazine and pirimicarb respectively, indicate a preference for pirimicarb adsorption onto the Nyex over atrazine. However, the R^2 values were very low where, R^2 = 0.264 and 0.132 for atrazine and pirimicarb, respectively. These data are very poorly represented by this model. The model which best fits the experimental data was the Freundlich equation, where R^2 = 0.881 and 0.953 for atrazine and pirimicarb, respectively. The values for *1/n* were 0.75 and 0.80 for atrazine and pirimicarb, respectively. The K_f values for atrazine and pirimicarb were 0.209 and 0.365 L/g, respectively. This reveals that when atrazine and pirimicarb are in the same solution, preferential adsorption of pirimicarb is observed.

The Freundlich isotherm model was determined to best represent the experimental data for the single and mixed compound adsorption isotherms. For atrazine and pirimicarb, the *1/*n and K_f values are both lower in the mixed vs. the single compound isotherms (Table 8.). Regarding the *1/n* values, this indicates that the degree of curvature of the line is slightly lower, meaning the adsorption intensity is lower (i.e.: at higher concentrations, less of the adsorbate was adsorbed onto the Nyex). This indicates that there is competitive adsorption occurring between atrazine, pirimicarb and NOM. This could mean that atrazine and pirimicarb are competing for similar adsorption sites even though they contain slightly different FGs and their 3D structure is different.

The K_f value for pirimicarb decreased by 73 % when compared to the single compound isotherm (Table 8.). This is a significant decrease. The decrease in the K_f value for atrazine is not as great as for pirimicarb but still significant (41 % decrease, Table 8.). This decrease indicates that the Nyex has a lower adsorption capacity for pirimicarb when atrazine and NOM is present in solution and likewise for atrazine. This is another indication that atrazine, pirimicarb and NOM are competing for the same binding sites.

Table 8. Comparison of the derived Freundlich parameters, 1/n and K_f from the single and mixed compound adsorption isotherm experiments				
	Pesticide	**Freundlich isotherm - Log Ce vs. Log qe**		
		R^2	1/n	K_f
Single compound isotherm	Atrazine	0.957	0.83	0.356
	Pirimicarb	0.982	0.85	1.375
Mixed compound isotherm	Atrazine	0.870	0.75	0.209
	Pirimicarb	0.917	0.80	0.365

Where the units for K_f are L/g

Ultimately, these results demonstrate that there is competitive adsorption occurring between atrazine, pirimicarb and NOM in solution. Thus, the presence of NOM can adversely affect the adsorption capacity of atrazine and pirimicarb. This has been demonstrated in similar studies for other MPs in which AC was the adsorbent material used (Smith and Weber, 1989). However, this is not surprising. Both atrazine and pirimicarb were present at concentrations that were 3 to 4 orders of magnitude lower than the concentration of NOM in the water (10.2 mg/L; Table 6.). Furthermore, NOM is a heterogeneous mixture of compounds of varying physio-chemical properties and molecular characteristics, making the likelihood of competition for binding sites on the Nyex even greater (Hu et al., 2014).

The results from this mixed compound, raw water, adsorption isotherm highlights that the NOM content is an important factor in removal of atrazine and pirimicarb from water. Methods to try and reduce the amount of NOM in the water before treatment, would greatly improve the adsorption of atrazine and pirimicarb onto the Nyex.

3. Experiment III – Nyex Saturation

3.1. Breakthrough Curve

A BTC illustrates the loading behaviour of the adsorbate in a column system (Aksu and Gonen, 2004). Adsorption is the accumulation of adsorbate molecules onto the surface of an adsorbent. In a fixed bed system in a column, the adsorbent which comes into contact with the adsorbate solution will saturate first, as this is where the adsorption initially takes place. As time passes and greater volumes of adsorbate solution pass through the bed, the adsorption zone moves along the fixed adsorbent bed in the column until it approaches the exit of the bed. When the concentration of the adsorbate at the

exit of the column is equal to the feed concentration, this indicates that the adsorption zone has moved through the entire column and the bed is now saturated (Ghorai and Pant, 2005). The longer the time required for the adsorbate concentration to break through the adsorbent bed, the higher the adsorption capacity and efficiency of the adsorbent (Adeyemi, 2017).

A breakthrough curve (BTC) is most commonly expressed in terms of normalised concentration against time. This is the ratio of effluent adsorbate concentration (C_t) to inlet/feed adsorbate concentration (C_0), (C_t/C_0), as a function of time (Aksu and Gonen, 2004) (Fig. 13.)

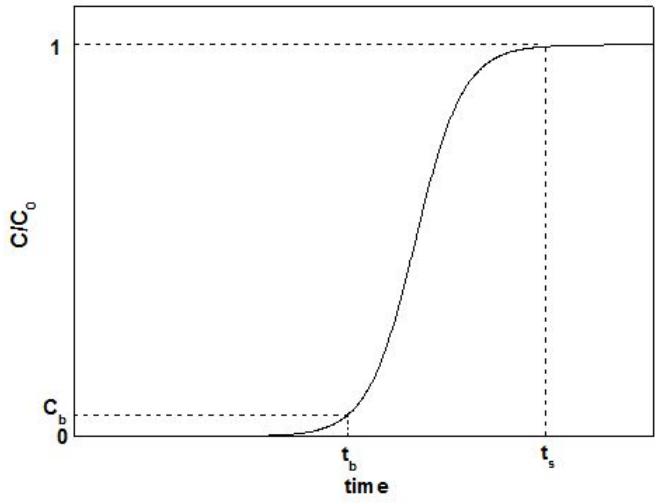


Fig. 13. Schematic representation of a break through curve. Source: (Oliveira et al., 2011)

At a concentration of C_b and a corresponding time of t_b the adsorbate has "broken through". At a time of 1 the bed is said to be exhausted or saturated. Once the adsorbate solution has broken through the ratio of the effluent to influent concentration will equal 1 and the curve will reach a plateau. Fig. 14. depicts the BTC for atrazine and Fig. 15. depicts the BTC for pirimicarb.

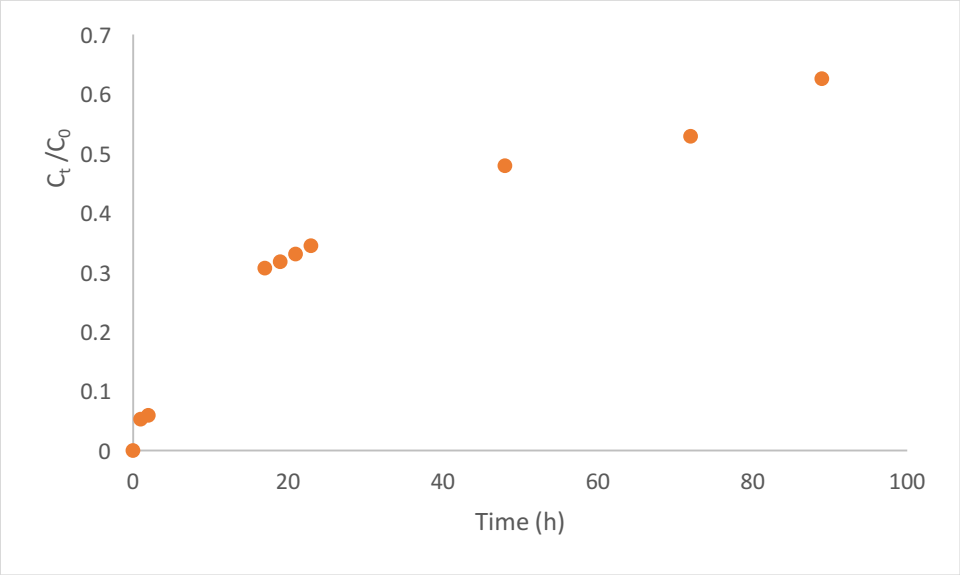


Fig. 14. Breakthrough curve for the recovery of atrazine from the solution using Nyex at a flow rate of 2 L/h, a bed height of 15 cm and initial concentration of 500 µg/L using an upward flow configuration

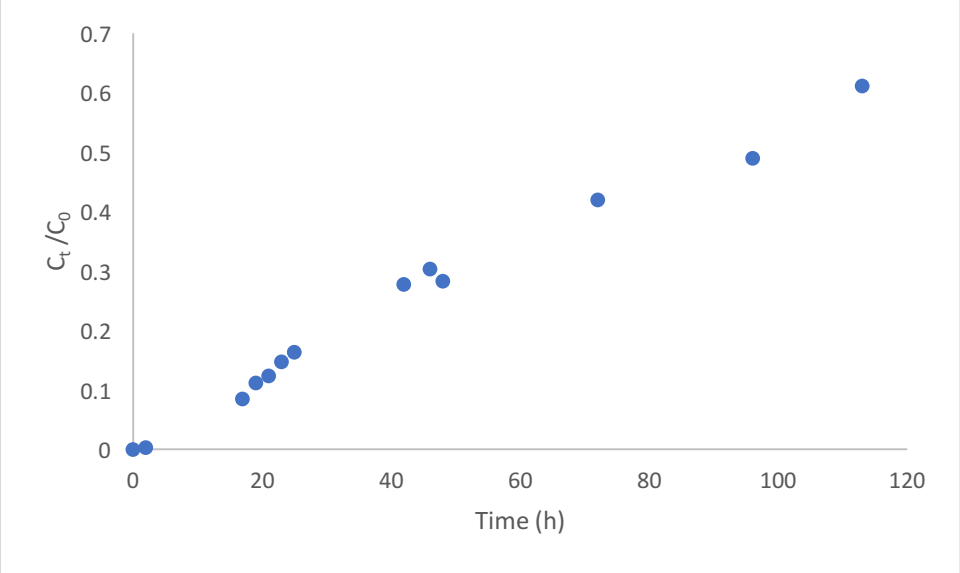


Fig. 15. Breakthrough curve for the recovery of pirimicarb from the solution using Nyex at a flow rate of 2 L/h, a bed height of 15 cm and initial concentration of 500 µg/L using an upward flow configuration

As can be observed from these BTCs, atrazine and pirimicarb did not reach saturation when using a influent concentration of 500 µg/L (i.e.: the effluent/ influent concentration did not reach 1). It was not possible to reach the time necessary to saturate the bed for atrazine and pirimicarb because the columns became blocked as something had started grow in the feed solution. However, it was possible to reach a point where the effluent concentration for atrazine and pirimicarb was approximately 300 µg/L (Table 9. and 10.) Therefore, an estimate of how much adsorbate needed to saturate the Nyex

in the column at 300 µg/L could be calculated for atrazine and pirimicarb using equation 10 (Table 9. and 10.).

Table 9. Estimation of the amount of atrazine adsorbed onto the Nyex using the breakthrough experimental data

Influent concentration = 500 µg/L
Flow rate = 2 L/h

Time (h)	**Effluent concentration (µg/L)**	**Amount of pirimicarb released in the effluent (µg)**
0	0	0
1	27	27
2	30	56
17	153	2745
19	159	625
21	165	648
23	172	674
48	239	10283
72	264	12091
89	313	9814
Total amount of atrazine found in the effluent (µg)		36,963 µg

Thus, the amount of atrazine adsorbed onto the Nyex = the amount that was fed into the column – the amount of atrazine released in the effluent

i.e.: amount fed into the column = 500 µg/L x 89 h x 2h/L

= 89,000 µg

Then, the amount of atrazine adsorbed onto the Nyex:

89,000 µg – 36, 963 µg = 52, 037 µg (52.04 mg)

Table 10. Estimation of the amount of pirimicarb adsorbed onto the Nyex using the breakthrough experimental data		
Influent concentration = 500 µg/L **Flow rate = 2 L/h**		
Time (h)	**Effluent concentration (µg/L)**	**Amount of pirimicarb released in the effluent (µg)**
0	0	0
2	2	5
17	43	686
19	56	199
21	62	235
23	74	270
25	82	312
42	139	3758
46	152	1165
48	142	590
72	210	8464
96	245	10921
113	306	9355
Total amount of pirimicarb found in the effluent (µg)		35, 959 µg

Thus, the amount of pirimicarb adsorbed onto the Nyex = the amount that was fed into the column – the amount of pirimicarb released in the effluent

i.e.: amount fed into the column = 500 µg/L x 113 h x 2h/L

= 113, 000 µg

Then, the amount of pirimicarb adsorbed onto the Nyex:

113, 000 µg – 35, 959 µg = 77, 041 µg (77.04 mg)

3.2. Artificial Pre-saturation

In order to saturate the Nyex at 300 µg/L, approximately 52 mg of atrazine and 77 mg of pirimicarb would be required. Thus, a mass of 3 mg of atrazine and 4 mg of pirimicarb was chosen to try to saturate the Nyex at a low µg/L concentration. When loading the pesticide compound onto the Nyex using these compound masses, they were found to saturate the Nyex at 3 µg/L and approximately 1 µg/L for atrazine and pirimicarb, respectively. Subsequently, during the ERG experiments and trials an atrazine feed solution of 3 µg/L and pirimicarb feed solutions of 0.7 and 0.9 µg/L were used.

4. Experiment IV – Electrochemical Regeneration

4.1. Electrochemical Regeneration Results

A bench top, flow through tubular unit was used to analyse and investigate the ERG of the Nyex and evaluate its ability to treat atrazine and pirimicarb at low µg/L concentrations. Thus, these results represent a series of trials/repeats done to investigate the performance of this system under an applied current. Prior to these ERG trials, the Nyex was artificially pre-saturated (i.e.: $C_t/C_0 > 1$) and then transfer into the tubular unit. This provided a base-line from which the performance of the system, under applied electric current, could be determined.

Two trials of the ERG of the Nyex with adsorbed atrazine were performed. The Nyex was saturated to 3 µg/L and the stock passing through the Nyex during the ERG was also 3 µg/L. A current of 0.125 A (0.66 mA/cm^2) was applied and the upward flow rate was 1 L/h. The destruction of atrazine during the ERG is represented in Fig. 16. The corresponding values of the graph are presented in Table 11., alongside the measured voltage and pH values of the effluent solution.

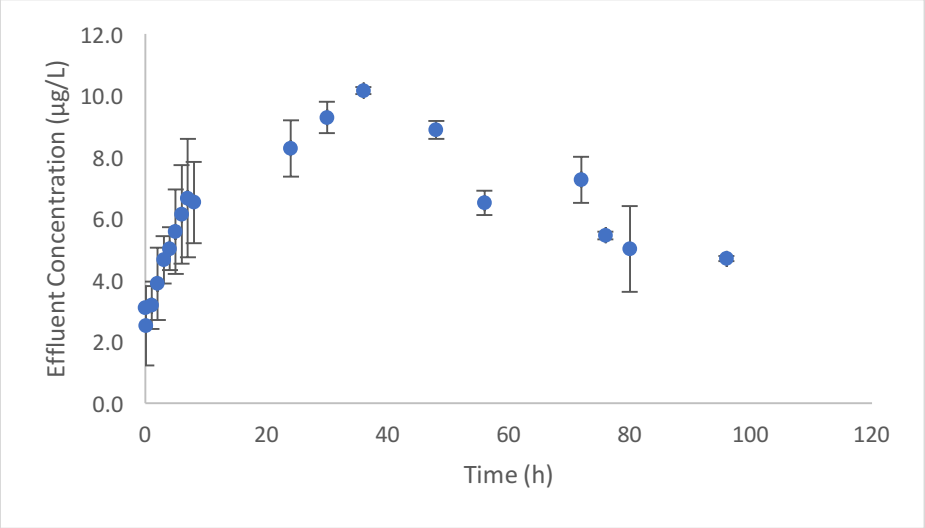


Fig. 16. Atrazine effluent concentrations during regeneration showing an average of two trials, where the error bars represent error to one standard deviation

The results show that in the effluent samples, the concentration of atrazine initially increased in both trials (Table 11.). After 36 h, the atrazine concentration in the effluent started to decrease back down towards the stock/fed concentration. The recorded voltage values were initially high but decreased steadily with time. The pH values are neutral (7.5) at the beginning of the ERG trials but, the pH

dropped with time to around pH 6. Finally, Nyex fines were observed in the effluent samples after 48 h in both trials.

Table 11. Atrazine effluent concentrations during electrochemical regeneration in the two separate trials conducted. pH and voltage values recorded in each trial are shown as averages with error represented as one standard deviation.

Time (h)	Trial 1. Effluent Conc.	Trial 2. Effluent Conc.	Average Effluent Conc. & Error	Average pH & Error	Average voltage & Error
0	3.1	3.1	3.1 ± 0	7.5 ± 0.0	8.3 ± 0.8
0.08	3.4	1.6	2.5 ± 1.3	7.3 ± 0.1	7.4 ± 1.7
1	3.7	2.6	3.2 ± 0.8	7.0 ± 0.2	6.5 ± 0.8
2	4.7	3.1	3.9 ± 1.2	6.6 ± 0.1	6.8 ± 0.1
3	5.2	4.1	4.7 ± 0.8	6.5 ± 0.1	6.3 ± 0.5
4	5.5	4.5	5.0 ± 0.7	6.0 ± 0.5	6.3 ± 0.1
5	6.6	4.6	5.6 ± 1.4	5.9 ± 0.4	6.1 ± 0.2
6	7.3	5.0	6.1 ± 1.6	6.1 ± 0.1	6.7 ± 0.5
7	8.0	5.3	6.7 ± 1.9	5.8 ± 0.6	5.9 ± 0.0
8	7.5	5.6	6.5 ± 1.3	6.0 ± 0.4	6.1 ± 0.5
24	8.9	7.6	8.3 ± 0.9	6.1 ± 0.0	5.7 ± 0.6
30	9.6	8.9	9.3 ± 0.5	5.8 ± 0.6	5.8 ± 0.4
36	10.3	10.1	10.2 ± 0.1	5.8 ± 0.6	5.8 ± 0.2
48	8.7	9.1	8.9 ± 0.3	6.0 ± 0.4	6.0 ± 0.0
56	6.8	6.2	6.5 ± 0.4	6.1 ± 0.3	5.9 ± 0.2
72	7.8	6.7	7.3 ± 0.7	6.1 ± 0.0	5.9 ± 0.2
76	5.4	5.5	5.5 ± 0.1	6.1 ± 0.1	6.1 ± 0.1
80	6.0	4.0	5.0 ± 1.4	6.3 ± 0.2	6.1 ± 0.1
96	4.6	4.8	4.7 ± 0.1	6.3 ± 0.3	6.0 ± 0.1

Effluent concentration in µg/L, voltage in volts (V)

Three trials of the ERG of the Nyex with pre-adsorbed pirimicarb were performed. The Nyex was saturated to 0.7 µg/L (trial 1) and 0.9 µg/L (trial 2 and 3) and the stock passing through the Nyex during the ERG was correspondingly 0.7 µg/L and 0.9 µg/L. A current of 0.125 A (0.66 mA/cm^2) was applied and the upward flow rate was 1 L/h. The destruction of pirimicarb during the ERG is represented in Fig. 17. The corresponding effluent concentration values of the graph are presented in Table 12., while pH and voltage values recorded during ERG of the Nyex are presented in Table 13.

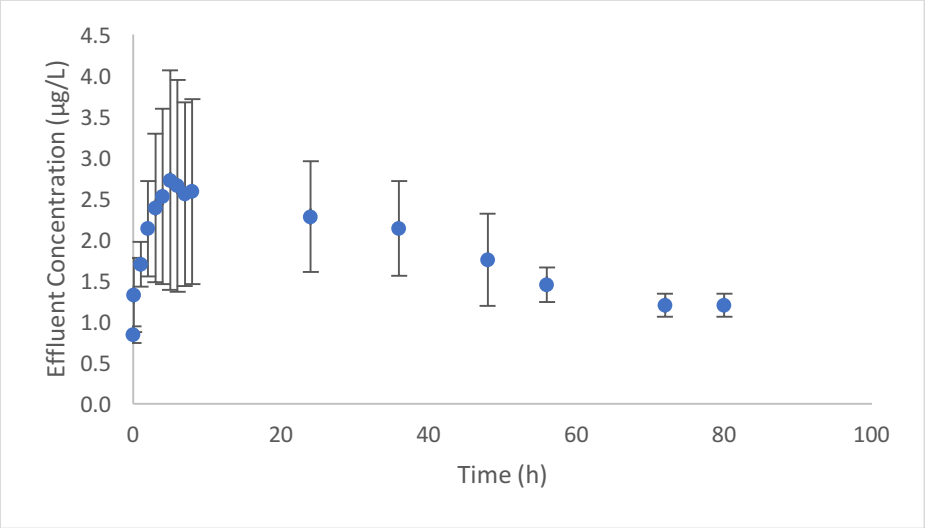


Fig. 17. Pirimicarb effluent concentrations during regeneration showing an average of three trials, where the error bars represent error to one standard deviation

There was greater variation about the mean in the effluent pirimicarb concentrations, in contrast to the ERG of atrazine (Fig. 16.). This was due to the variation in the pirimicarb concentration measured in the effluent samples (Table 12.). Similarly to the atrazine trials, there was an initial increase in the concentration of pirimicarb in the effluent samples in all three trials. However, this initial increase in concentration, varied in the three trials and follows the order: trial 1> trial 3> trial 2.

Table 12. Pirimicarb effluent concentrations during electrochemical regeneration in the three separate trials conducted. Effluent concentrations are shown individually and as an average with error represented as one standard deviation.

Time (h)	Trial 1. Effluent Conc.	Trial 2. Effluent Conc.	Trial 3. Effluent Conc.	Average Effluent Conc. & Error
0	0.8	0.9	0.9	0.8 ± 0.1
0.08	1.0	1.8	1.1	1.3 ± 0.5
1	1.8	1.4	1.9	1.7 ± 0.3
2	2.6	1.5	2.4	2.1 ± 0.6
3	3.2	1.4	2.5	2.4 ± 0.9
4	3.6	1.4	2.5	2.5 ± 1.1
5	4.1	1.4	2.6	2.7 ± 1.3
6	4.0	1.4	2.5	2.7 ± 1.3
7	3.7	1.5	2.5	2.6 ± 1.1
8	3.7	1.5	2.5	2.6 ± 1.1
24	3.0	1.8	2.0	2.3 ± 0.7
36	2.8	1.8	1.8	2.1 ± 0.6
48	2.4	1.4	1.5	1.8 ± 0.6
56	-	1.3	1.6	1.5 ± 0.2
72	-	1.3	1.1	1.2 ± 0.1
80	-	1.3	1.1	1.2 ± 0.1

Effluent concentrations in µg/L

Likewise to the ERG of the Nyex with pre-adsorbed atrazine, in all the trials, the amount of pirimicarb measured in the effluent samples decreased. For trial 1 and 3 the decrease was observed after 8 h and after 36 h for trial 2. However, for both atrazine and pirimicarb the effluent concentrations never went back down to the stock/fed concentration. Again, Nyex fines were observed in the effluent samples after 48 h in all three trials. Trial 1 was terminated after 48 h due to the presence of Nyex fines however, trial 2 and 3 were kept running even after fines had been observed in the effluent samples. The recorded voltages and pH values in trial 1 and 3 were similar. The voltages in these trials were initially high (approx. 9 V) and decrease over time. The pH values were neutral (approx. 7.5) at the beginning of each trial, but the pH dropped with time to around pH 6 (Table 13.).

However, a different trend was observed for the recorded voltages and pH values in trial 2 vs.trial 1 and 3. In trial 2, the voltages recorded were half of those measured in trial 1 and 3. Furthermore, the pH values remained neutral.

Table 13. Voltages and pH values recorded during the electrochemical regeneration of the pirimicarb-adsorbed Nyex in the three separate trials conducted.

Time (h)	Trial 1.		Trial 2.		Trial 3.	
	Voltage	pH	Voltage	pH	Voltage	pH
0	-	7.5	-	7.7	-	7.7
0.08	8.9	7.5	4.0	7.4	8.8	7.3
1	9.2	6.8	3.5	7.3	8.2	6.8
2	8.7	6.6	3.6	7.4	7.9	6.6
3	8.9	6.6	3.9	7.5	7.6	6.5
4	8.0	6.4	4.1	7.5	7.3	6.4
5	8.1	6.4	4.3	7.4	7.0	6.5
6	7.8	6.5	4.7	7.4	7.4	6.7
7	7.5	6.5	5.1	7.5	6.6	6.6
8	7.3	6.5	5.0	7.5	6.9	6.5
24	6.6	6.4	4.8	7.2	6.5	6.6
36	6.5	6.5	4.5	7.3	6.3	6.6
48	6.2	6.5	4.2	7.0	5.4	6.4
56	-	-	4.1	7.2	5.6	6.4
72	-	-	4.1	7.1	5.7	6.3
80	-	-	4.2	7.2	5.8	6.5

voltage in volts (V)

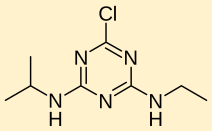
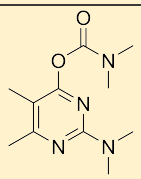
In an ideal ERG process, the adsorbent should be regenerated while simultaneously fully oxidising the adsorbed species, resulting in no adsorbate molecules being transferred into solution (Hussain, 2012). In this study, the ERG results demonstrated that atrazine and pirimicarb, at trace level concentrations, were not effectively treated and destroyed. Furthermore, these results illustrate that adsorbate molecules have been transferred into the liquid phase during ERG. This demonstrates that atrazine and pirimicarb are desorbing from the Nyex surface when there is a current applied. This accounts for the initial increase in the concentration of atrazine and pirimicarb in the effluent samples.

To evaluate why this desorption is occurring it is necessary to understand the chemistry of both compounds and thus the way in which they interact with the Nyex during adsorption (without current) and during ERG (with current).

4.2. The Chemistry of Atrazine and Pirimicarb

At a neutral pH (e.g.: 7.5) atrazine and pirimicarb are neutral species in water. The nature of the molecule i.e.: its acidity/ basicity, will determine its ionic form at different pH values. Atrazine and pirimicarb are both bases. Since they're both basic molecules the values of the base dissociation constant (pK_b) and the conjugate acid dissociation constant (pK_{ah}) provide information on the ratio/distribution of charged to uncharged species in solution. Table 14. shows the molecular structures and corresponding pK_b and pK_{ah} values of atrazine and pirimicarb (Whitacre, Lupul et al., 2015).

Table 14. Atrazine and pirimicarb molecular structures and dissociation constants

Pesticide	Atrazine	Pirimicarb
Molecular Structure		
Base Dissociation Constant (pK_b)	12.3	9.6
Conjugate Acid Dissociation Constant (pK_{ah})	1.7	4.4

For a basic molecule in an aqueous environment:

$$B + H_2O \leftrightharpoons HO^- + BH^+$$

Where, *B* is the base and BH^+ is the conjugate acid.

K_b, is the base ionisation constant and represents the equilibrium constant of bases in aqueous solutions. It is used to predict the extent of base dissociation and thus the strength of the base.

$$K_b = \frac{[BH^+][HO^-]}{[H_2O]}$$

Thus, the larger the K_b value the stronger the base and the greater the dissociation. K_b values are expressed as the negative log of K_b (i.e.: pK_b) thus, the lower the pK_b, the stronger the base. Atrazine and pirimicarb have pK_b values of 12.3 and 9.6 respectively, which makes them both relatively weak bases (Table 14.).

Depending on the pH of the aqueous solution, atrazine and pirimicarb can exist in different ionic forms. The possible states of atrazine and pirimicarb are shown in Fig. 18.

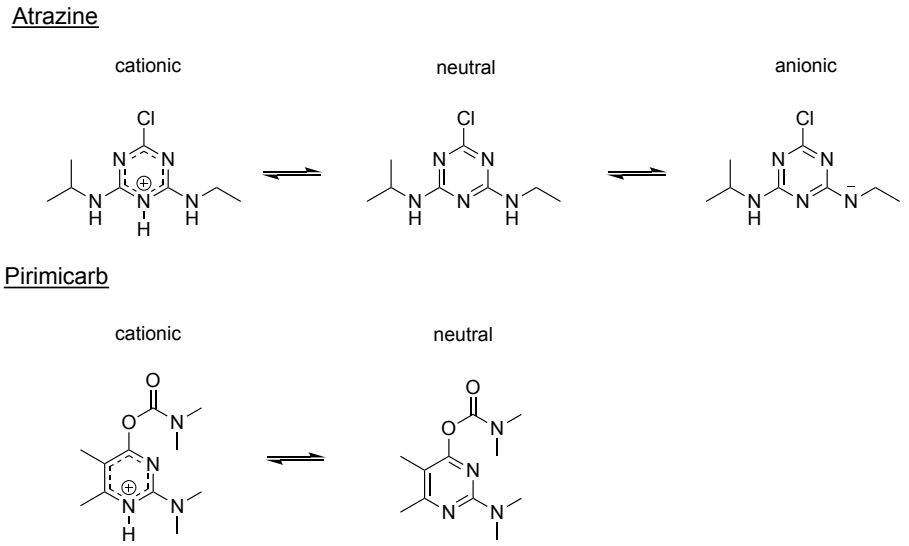


Fig. 18. States of atrazine and pirimicarb

Furthermore, the distribution of these states at different pH values is illustrated in Fig. 19. This diagram illustrates the relationship between the distribution of the various states of atrazine and pirimicarb at different pH values. This figure highlights that two equilibrium states exist:

- Between the cationic and neutral species (at lower pH values)
- Between the neutral and anionic species (at higher pH values)

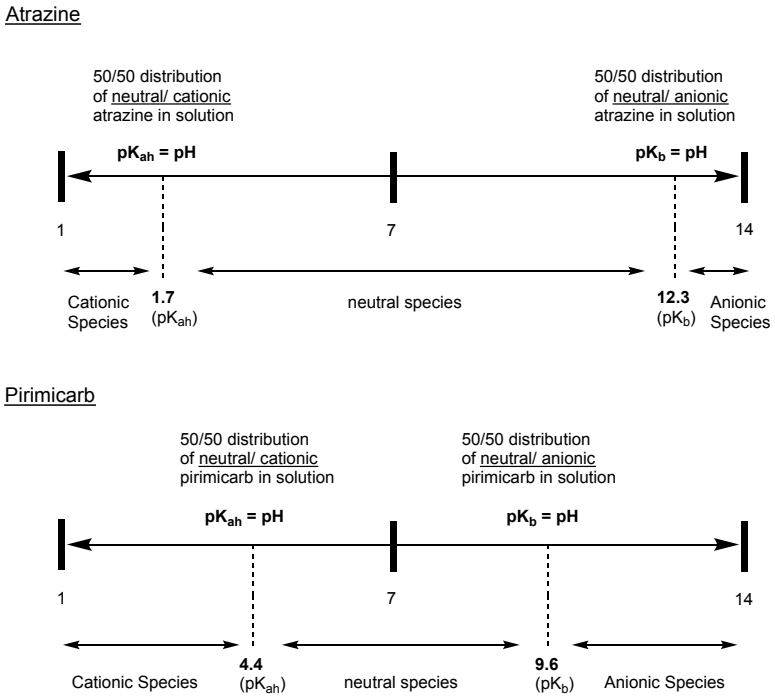


Fig. 19. The possible states of atrazine and pirimicarb and their distribution over the whole pH range (1 -14)

For bases if:

- pH > pK_b – deprotonated and anionic (negatively charged)
- pH < pK_b – neutral
- pH = pK_b – 50/ 50 distribution of neutral to anionic species

The pK_b of atrazine is very high (12.3), making it a very weak base. This indicates that atrazine will only be deprotonated at very high pH values (when there is a large presence of OH^- ions in solution). When the pH < pK_b, the higher ratio of H^+ ions means that atrazine will be in its neutral form. In regards to pirimicarb, apart from the methyl groups, there are no other extractable H atoms (i.e.: pirimicarb has no acidic proton). In order to remove a H atom from pirimicarb (i.e.: from a methyl group) a strong base would be required. Thus, pirimicarb also has a large pK_b value (9.6). Similarly to atrazine, this large pK_b value means that in order for pirimicarb to be deprotonated and anionic the external pH has to be high.

However, in these experiments the aqueous solution becomes acidic i.e.: the there is a higher presence of H^+ ions in solution from the anodic oxidation of water. As shown in Fig. 19. an equilibrium also exists between the neutral and cationic species. This equilibrium occurs at lower pH values where

the molecule becomes protonated and cationic. When the molecule is protonated (i.e.: the conjugate acid, BH^+), the dissociation constant of that protonated species is known as its pK_{ah}.
Thus, for bases if:

- $pH < pK_{ah}$ – protonated and cationic (positively charged)
- $pH > pK_{ah}$ – neutral
- $pH = pK_{ah}$ – 50/ 50 distribution of neutral to cationic species

The two most basic nitrogen (N) sites on pirimicarb are those on the ring and are the sites most likely to be protonated. The most basic N has a pK_{ah} value of around 4.4. Since the pK_b value is above the effluent pH values, for the purpose of this dissertation, there are two possible pirimicarb forms, neutral and cationic. Protonation of the neutral molecule to its corresponding cationic form is possible, if the pH decreases until the pH reaches the pK_{ah} threshold of the basic N atom. Thus, it is expected that at a pH of 4.4, that there will be a 50/50 distribution of the cationic and neutral species in solution. Decreasing this pH further, the presence of H^+ ions increases and the equilibrium will shift from the neutral species to the cationic species. Thus, in water, at a pH of 7.5, pirimicarb will be largely in its neutral form (Fig. 19.).

For atrazine the site at which protonation occurs is more complex than pirimicarb, as it has more N atoms which are all likely to be protonated (five vs. two). Therefore, at a very low pH there can be multiple mono-protonated species. However, the most basic N (i.e.: the N atom most likely to be protonated) is in the centre of the ring. This is the most stable site for protonation because the positive charge can be delocalised over three N atoms. This occurs through the delocalisation of the lone pair of electrons on the N atoms (from the ethyl- and isopropyl-amino side chains) into the ring system. Although atrazine has three possible forms (anionic, neutral and cationic) for the purpose of this dissertation, only the neutral and cationic forms are taken into account. The pK_{ah} of atrazine is 1.7, thus even in acidic conditions, where the pH is around 3/4, most of the species will be in its neutral form. In very acidic conditions, at pH 1.7 and below, there will be an equilibrium shift from the neutral to the cationic species. However, once this site is protonated, the H atom is considered to be very acidic. As a result, it is easily removed as it would go back to the neutral species, which is more stable and favourable. Hence, you require a harsh acidic environment to protonate it.

Thus, for the purpose of this dissertation, atrazine and pirimicarb will both be neutral species at pH 7.5. Atrazine will only be protonated and cationic at very low pH values while pirimicarb will be protonated at less harsh acidic conditions.

4.3. Molecular Interaction with the Nyex during Adsorption

The adsorption and thus removal of organic compounds is strongly dependent on the carbon surface chemistry of the adsorbent (Nkrumah-Amoako et al., 2014, Lupul et al., 2015). The carbon surface properties are governed mostly by the presence of oxygen (O) and N FGs (Mattson et al., 1969). Furthermore, the ionisation of the adsorbate molecule is important, as it will influence the interactions it will have with the various organic FGs on the Nyex surface. In this study, during the adsorption process, the pH of the atrazine and pirimicarb solutions were neutral and hence both compounds were in their neutral form and uncharged.

Several groups have reported on the different molecular interactions responsible for the adsorption of atrazine onto various adsorbents. These predominantly highlight the role of non-covalent interactions i.e.: a mix of π-π stacking interactions, van der Waals forces and electrostatic interactions (Ledesma et al., 2014). For example, a study by Lupul et al., (2015) described that the adsorption of atrazine onto AC mainly involved π – π interactions between the atrazine π electron ring and the π electrons of the graphene layers of AC. This mechanism of adsorption was also believed to contribute substantially to the adsorption of atrazine onto Nyex 100 (Brown et al., 2004a). Both atrazine and pirimicarb have aromatic rings consisting of π conjugated electrons, which are delocalised in the aromatic ring. Thus, π-π stacking interactions of the aromatic rings of atrazine and pirimicarb, with other conjugated systems on the adsorbent, could likely be a predominant interaction accounting for the adsorption of these two compounds onto the Nyex. However, H bonding molecular interactions are also highly likely to occur between the organic FGs on the Nyex surface and atrazine and pirimicarb. For example, atrazine is capable of forming hydrogen bonds (HBs) with other HB acceptor/donator moieties in other molecules (Welhouse and Bleam 1993). These authors report that the para N in the atrazine ring is a HB acceptor while the ethylamino and isopropylamino side chains can be a HB donors (Welhouse and Bleam, 1993, Lupul et al., 2015). Additionally, atrazine has been known to form HBs with carboxyl and phenolic FGs (Davies and Jabeen, 2003). Likewise, pirimicarb has four N and two O atoms capable of being HB acceptor sites.

Nkrumah-Amoako et al., (2014) reported that prior to oxidation, the predominant FGs determined to be on the surface of the Nyex were:

- Hydroxyl FGs
- Phenolic FGs
- Carbonyl FGs

The presence of these groups indicate that H bonding (van der Waals forces) and π- π interactions can form between the FGs on the surface of the Nyex and atrazine and pirimicarb.

When there is an interaction of two π conjugated electron systems, two factors will influence the stability of such complexes (Mattson et al., 1969):

- The electron density in the donor
- The electron affinity of the acceptor

The electron density of an aromatic ring is strongly influenced by the nature of the substituent groups (Mattson et al., 1969). For example, if the hydroxy group on the phenol is in the para position, it behaves as an electron donating group. In this case, phenol would be a good candidate as an electron donor in a π system. The electronegative chlorine atom on atrazine would cause an electron withdrawing effect, pulling electrons from the π conjugated ring. Thus, a stable and strong interaction of the two π systems between phenol and atrazine could likely occur. Similarly, for pirimicarb, the amide group would have an electron withdrawing effect, enhancing the π-π stacking interaction of its own aromatic ring with phenol. Mattson et al., (1969) also suggested that a π interaction, between the carbonyl FGs on the surface of AC and the adsorbate aromatic ring, could be formed. In this donor – acceptor complex the carbonyl O acts as the electron donor while the aromatic ring acts as the electron acceptor. This could also occur in the present study as both atrazine and pirimicarb would act as the electron acceptors in the complex.

Lastly, the Nyex surface contains a collection of organic FGs which contain O and H atoms (phenol, hydroxyl and carbonyl groups). Phenol and hydroxyl groups can readily form HB donor – acceptor interactions with O. Thus, H bonding is a likely surface interaction responsible for the adsorption of atrazine and pirimicarb. The results from the adsorption studies (Experiment II) have consistently indicated that Nyex has a lower adsorption capacity for atrazine i.e.: it is not adsorbed as well as

pirimicarb. This may be rationalised by the difference in the extent and strength of the H bonding occurring between atrazine and pirimicarb and the adsorbent FGs. The electronegativity of O is greater than that of N. Thus, O – H bonds will form stronger HB donor - acceptor interactions in comparison to N – H bonds. Atrazine contains five N atoms, two of which act as H donors and three as H acceptors. Whereas, pirimicarb contains two O atoms and four N atoms, all of which act as HB acceptors. There are more sites available for H bonding on pirimicarb as well as O atoms. This could contribute to the higher Nyex adsorption capacity toward pirimicarb.

4.4. The Effects of Electrochemical Regeneration on the Nyex and on Adsorption

ERG which leads to electrochemical oxidation, will alter the surface chemistry of the Nyex (Nkrumah-Amoako et al., 2014). The changes will specifically be observed to modify the O containing FGs on the carbon surface (Mattson et al., 1969, Mehta and Flora, 1997, Lupul et al., 2015) and are believed to give the Nyex new surface properties (Nkrumah-Amoako et al., 2014). (Coughlin, 1968) and (Mehta and Flora, 1997) both reported that the adsorptive capacity of AC for phenol was reduced after anodic oxidation. Therefore, the hypothesis that there is a relationship between the modification of the surface chemistry of the electrochemically oxidised carbon and its ability to continue to adsorb organic compounds, is highly credible (Nkrumah-Amoako et al., 2014). This could be why atrazine and pirimicarb desorb from the Nyex during ERG, rather than being destroyed or mineralised on the Nyex surface.

In the present study, the desorption of atrazine and pirimicarb is likely to be due to a mixture of contributing factors. These include:

- Modifications of the Nyex surface during ERG
- The stability of the molecular interactions being compromised
- Significant changes in the localised pH around the Nyex
- The experimental method chosen to pre-saturate the Nyex for the ERG experiments

During anodic oxidation, the Nyex surface transfers electrons to the cathode and results in (Brown et al., 2004b, Brown and Roberts, 2007, Nkrumah-Amoako et al., 2014):

- Oxidation of the organic contaminant
- Oxidation of water

- Oxidation of the surface of the Nyex

This electron transfer results in a temporary net positive charge surrounding the Nyex. Another important feature of the ERG of the Nyex, is the change in the pH of the solution. Before ERG (i.e.: during adsorption) the pH is neutral and atrazine and pirimicarb are in their neutral forms. However, during treatment the pH drops to approx. 6/5. This decrease in pH is as a result of the oxidation of water in the anodic compartment, which will increase the amount of H^+ ions in solution (Brown et al., 2004b). However, simultaneously in the cathodic compartment, the reduction of water is increasing the pH (Brown et al., 2004b). Both compartments are separated by a membrane and so the water from two compartments will mix on exiting the unit. Therefore, the pH measured in the effluent samples will be a mixture of the anodic and cathodic solution pH and will not give the exact pH value of the solution around the Nyex. Thus, the localised pH around the Nyex is likely to be significantly lower than the measured values (Asghar, 2011). However, this is likely to have a greater effect on pirimicarb, as its corresponding pK_{ah} value is higher than atrazine's. Thus, a greater distribution of the pirimicarb cationic species in solution would be expected.

Studies on the effect of ERG and thus electrochemical treatment on the Nyex surface have been conducted by (Nkrumah-Amoako et al., 2014). Herein, they report that ERG of the Nyex led to:

- A significant decrease in the presence of phenolic FGs
- An increase in the formation of carboxylic acid FGs
- A significant decrease in the presence of hydroxyl FGs

The decrease of phenolic compounds on the Nyex surface is significant. This would indicate that the π interactions between the phenolic compounds and atrazine and pirimicarb would be lost. As this was considered to be a major way in which these compounds adsorb onto the Nyex surface, it is likely that this could be a contributing factor towards the desorption of both compounds. Furthermore, for the remaining phenolic groups, Mattson et al., (1969) reported that the presence of additional acidic surface O groups, produced from the oxidation of carbon, will withdraw electrons from the phenolic π - system. They report that this would affect the stability of the π system due to the shift in electron density. In addition to this, the pH of the atrazine and pirimicarb solution is decreasing, due to the oxidation of water. This will shift the equilibrium and ratio from the neutral species to the cationic species, in particular for pirimicarb. Protonation will result in a full positive charge in the ring and will affect the aromaticity of the ring (Fig. 18). Thus, the electron deficient phenol and cationic pirimicarb

molecule will repel one another, destabilising and breaking the π interaction. This could contribute to the desorption of pirimicarb during ERG.

As mentioned above, electrochemical oxidation of the Nyex surface leads to an increase in the formation of carboxylic acid groups. This could have occurred through the oxidation of aldehyde FGs present on the Nyex surface to carboxylic acid (Mattson et al., 1969, Brown et al., 2004a). The original π interactions between the Nyex carbonyl FGs and atrazine and pirimicarb could be weakened by the transformation of these carbonyl FGs. The reason being that the conjugated O atom on a carboxylic acid has a lower dipole moment than the carbonyl O atom of an aldehyde moiety. The dipole moment is the determining factor for the strength of the donor – acceptor complex formed. Thus, a carbonyl group provides a stronger π interaction (Mattson et al., 1969). Hence, the electrochemical oxidation of the Nyex surface could reduce the adsorption of atrazine and pirimicarb by reducing this dipole moment.

ERG decreases the amount of hydroxyl groups present on the surface of the Nyex. This would reduce the amount of H bonding which is thought to occur during adsorption. As this was considered to be a main mechanism for the adsorption of atrazine and pirimicarb, it is likely to contribute to their desorption. This is supported by a study done by Mattson et al., (1969). They reported that there was a simultaneous decrease in the presence of hydroxyl groups and reduced adsorptive performance of phenol onto AC, after oxidative treatment of the sorbent.

Another important factor, which could contribute to the desorption of atrazine and pirimicarb, is the decrease in the pH. This decrease in pH could contribute in various ways including increasing the solubility of atrazine and pirimicarb. Acidic conditions will create more cationic species and greater solubility of compounds occurs when they're charged (e.g.: protonated) and thus more polar and hydrophilic. This can lead to desorption from the adsorbent due to the formation of stronger adsorbate – water bonds. This increase in solubility has been described and reported by Dabrowski et al., (2005) for phenol adsorption onto AC. The change in pH could also contribute to the desorption of atrazine and pirimicarb in another way. In acidic conditions, there is an equilibrium shift from the neutral to the cationic species. Simultaneously, the Nyex is being oxidised from the ERG and is transferring electrons to the cathode. As a result, the Nyex goes from being neutral to temporarily positively charged. This would result in a repulsive electrostatic effect between the positively charged Nyex and cationic atrazine and pirimicarb adsorbate molecules. Thus, this may also be a possible major

contributing factor to the desorption effect of atrazine and pirimicarb. However, again this is more likely for pirimicarb than atrazine.

Analysing the results, what stands out is how rapidly this desorption effect was observed. It was immediate and visible in the first effluent samples taken after 5 min. Changes in pH and modifications of the Nyex surface FGs would not be as instant and quick as the effect an applied current would have. All the discussed factors could likely have contributed and influenced the desorption of atrazine and pirimicarb. However, the applied current itself (and not just the side-effects of the current) is also likely to play an important role in the desorption of both compounds. This is supported by the comparison of the voltage values recorded in the three trials of the pirimicarb ERG results (Table 13.). In trial 1 and 3 the initial voltages were double that of trial 2 and the amount of desorption observed in trial 2 was notably less than in trial 1 and 3 (Table 12.). This illustrates that the voltage and current play a role in the extent of desorption of both atrazine and pirimicarb. This effect is termed "electro-desorption". Electro-desorption is used as the first key step in the regeneration of GAC. It is reported that a higher electric current would accelerate the desorption of the contaminant from the GAC surface. Furthermore, it has been shown to be time dependent i.e.: the longer the RG time the greater the extent of desorption (Narbaitz and Karimi-Jashni, 2009).

Another observation which supports this theory is that the extent of desorption of both atrazine and pirimicarb is similar. Without taking the applied current into account, the key factors thought to be responsible for the desorption of atrazine and pirimicarb are:

- Loss of stability of the intermolecular interactions
- Increased solubility
- Repulsive electronic effects

However, as previously discussed, the acidic conditions would have to be very harsh for atrazine to be protonated. These harsh conditions were likely not attained in these experiments. Thus, ERG should have had a greater effect on pirimicarb and thus one would expect more pirimicarb desorption. However, this was not observed. The extent of desorption of both atrazine and pirimicarb was similar, if indeed slightly higher for atrazine. This further indicates that the applied current itself was also likely to be partly responsible for the desorption of both compounds.

The desorption of atrazine and pirimicarb from the Nyex surface was unexpected. Other Nyex ERG studies using other organic compounds have not observed this desorption effect (Brown 04, Brown 07, Ashgar 12, Nabeerasool 15). However, there are some important differences in these sets of ERG experiments. These include: the method of artificial pre-saturation of the Nyex prior to ERG and the unit in which Nyex ERG was carried out.

Time limitations of this project led to the decision to artificially pre-saturate the Nyex prior to commencing the ERG trials. This method of artificially pre-saturating the Nyex was not chosen in any of the above referenced studies (as explained in chapter 2 section 2.3.). However, this was the only viable and practical option for this project. It could be that artificial saturating the Nyex lead to the desorption of both pesticides. Secondly, ERG of the Nyex was conducted in a proto-type tubular unit and not the commercialised Organics Destruction Cell (ODC) unit. As this is an early prototype, and with the limited time allowed in this project, optimisation of the operating conditions could not be explored to improve the results.

Ultimately, there are many different factors which could play a role in the desorption of atrazine and pirimicarb. While all are plausible and could have contributed, more work needs to be done to assess the contribution of each factor to draw a definite conclusion. Furthermore, importantly the methodology should be reviewed and improved to see whether other methods could prove more successful.

Finally, after the initial desorption, there was some reduction in the amount of atrazine and pirimicarb detected in the effluent samples (Fig. 16. and 17.). This reduction may be due to attrition of the Nyex. Particles were observed in the effluent samples after 48 h and the amount of fines observed increased with time. This is an indication that the Nyex particles have started to erode under the applied current during ERG of the Nyex. This attrition increases the Nyex's surface area and promotes further adsorption. This effect was also observed on the Nyex 1000 (Nkrumah-Amoako et al., 2014). However, in the present study there was also the formation of atrazine and pirimicarb DPs (discussed below). Therefore, it is likely that this decrease in the effluent concentration of atrazine and pirimicarb is due to a combination of new adsorption and the oxidative destruction of both compounds.

5. Experiment V – Degradation Product Formation

In the present study, the tentative identification of the atrazine and pirimicarb DPs formed via reactions with ·OH radicals during the electrochemical oxidative processes were assessed using a HPLC/MS based method. The formation of two DPs was observed for atrazine, while pirimicarb formed one DP. Due to time restrictions, the DPs in this study were not identified through the use of authentic standards. Thus, all values corresponding to the formation of DPs are peak areas and response values. However, in this dissertation a tentative identification could be made on the structure of the unknown DP. This was based on their exhibited *m/z* ratios and RTs and was compared to the *m/z* ratios of atrazine DP formed in other AOP studies.

5.1. Atrazine Degradation Products

The DPs of atrazine were tentatively identified as de-ethyl-deisopropyl-atrazine (DEDIA) and 2-chloro-4-ethylimino-6-isopropylamino-*s*-triazine (ATRA-imine). The DPs of atrazine with their corresponding *m/z* ratios and RTs are shown in Fig. 20.

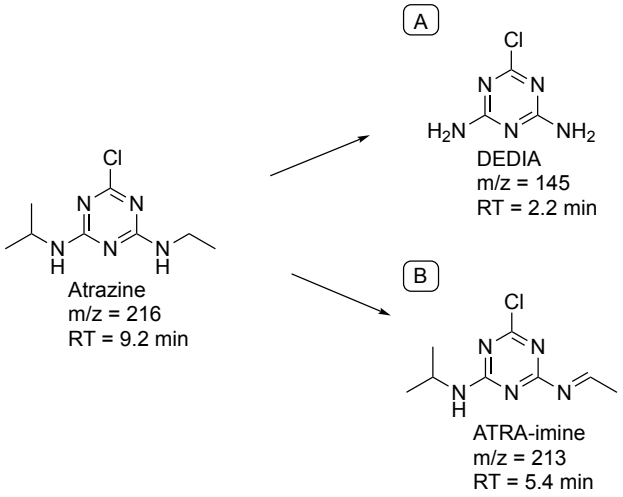


Fig. 20. Molecular structures of the atrazine DPs with their corresponding *m/z* ratio and RTs

Table 15. shows the relative amounts of DP formation of DEDIA and ATRA-imine. ATRA-imine was detected after the current had been turned on for 5 min in the two atrazine ERG trials. DEDIA was formed slightly slower as it was detected after 1 hour in trial 1 (T1) and after 2 hours in trial 2 (T2).

Both the response values of DEDIA and ATRA-imine show that there was an initial increase in the formation of these DPs, which then began to decrease after 8 h for DEDIA in T1 and T2. While the formation/ detection of ATRA-imine started to decline after 48 and 36 h in T1 and T2, respectively. The relative amounts of DEDIA formed in T1 and T2 and ATRA-imine formed in T1 and T2, were similar.

Table 15. Formation of atrazine degradation products (DEDIA and ATRA-imine) and corresponding recorded voltage values.

	Trial 1.			Trial 2.		
Time (h)	DEDIA	ATRA-imine	Voltage	DEDIA	ATRA-imine	Voltage
0	0	0	-	0	0	-
0.08	0	105	8.8	0	103	7.7
1	102	174	8.6	0	163	6.2
2	112	161	7.1	0	155	5.9
3	105	179	6.8	59	173	6.7
4	118	190	5.9	114	186	6.6
5	160	163	6.2	187	154	6.4
6	217	201	6.2	147	208	5.9
7	166	157	7.0	208	148	6.3
8	178	169	5.9	273	173	5.9
24	77	169	5.7	250	177	6.4
30	54	169	5.2	238	179	6.1
36	0	146	5.5	95	137	6.1
48	67	149	5.6	87	95	5.9
56	49	114	6.0	0	107	6.0
72	55	114	6.0	78	102	5.7
76	0	95	6.0	0	114	5.7
80	0	122	6.1	0	151	6.0
96	0	131	6.0	0	139	6.2

Values are expressed as response x 10^{-3}, where response is defined as peak area count of the metabolite/peak area count of the internal standard. The voltage was measured in volts.

DEDIA (Fig. 20.; A) is an atrazine DP which has been identified in other electrochemical AOPs (Acero et al., 2000, Balci et al., 2009, Komtchou et al., 2016, Komtchou et al., 2017). In comparison with other atrazine DPs formed in these studies, DEDIA was one of the more resistant to electrochemical oxidation and was broken down more slowly. The slow destruction of DEDIA indicates that it has a low reactivity with ·OH radicals (Balci et al., 2009). DEDIA is formed through the de-alkylation of the ethylamino and isopropylamino atrazine side chains. Balci et al., (2009) proposed a mineralisation pathway of atrazine by ·OH radicals, part of which included the formation of DEDIA. This mechanism for the formation of DEDIA is shown in Fig. 21. This mechanism illustrates that DEDIA is formed

through two other intermediates, de-isopropyl-atrazine (DIA) and de-ethyl-atrazine (DEA). Both DIA and DEA are formed through the *N*-dealkylation of the isopropylamino side chain and the *N*-dealkylation of the ethylamino side chain, respectively. When both side chains are dealkylated to the free amino group, DEDIA is formed (Fig. 21.)

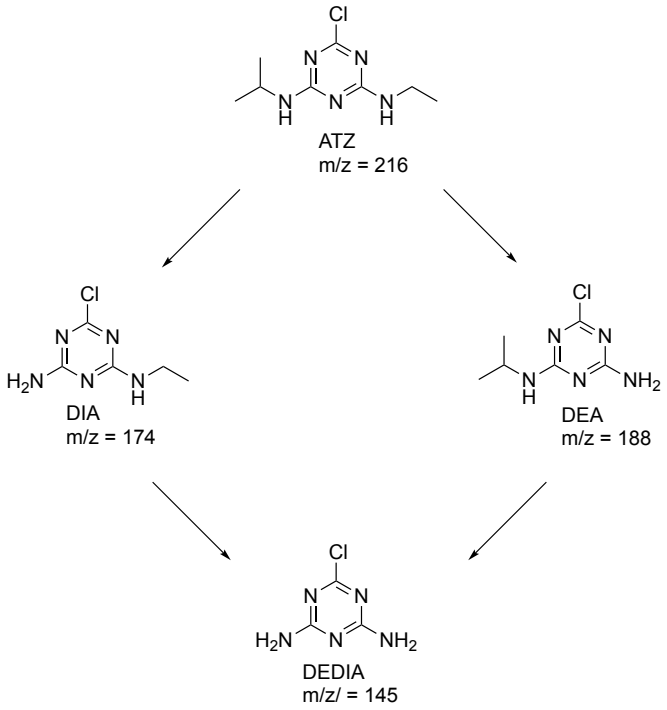


Fig. 21. Proposed reaction pathway for the formation of DEDIA

In the present study, DIA and DEA were not detected. However, Balci et al., (2009) reported that the maximum concentrations of DIA and DEA were measured after 8 and 30 min, respectively. Furthermore, the time for complete destruction of DIA and DEA was 20 and 140 min, respectively. This highlights that ·OH radical attack on atrazine, forming DIA and DEA, was very quick. As was the subsequent ·OH radical attack on DIA and DEA forming DEDIA. In the present study, it seems likely that DEDIA was formed through the dealkylation of DIA and DEA. DIA and DEA may not have been detected due to a combination of different factors. Firstly, the concentration of atrazine in solution is very low and depending on the sensitivity of the LCMS method, they may not have been below the limit of detection. Secondly, ·OH radicals are highly reactive and unpredictable and in this study, could have reacted quicker with DIA and DEA to form DEDIA.

A proposed mechanism for the dealkylation of both atrazine side chains is shown in Fig. 22. Acero et al., (2000) reported that the ethylamino group was found to be four times more reactive than the isopropyl group, when under ·OH radical attack. Thus, this proposed mechanism starts with the *N*-

dealkylation of the atrazine ethylamino side chain to form DEA, which is then further dealkylated to DEDIA. However, DEDIA can also be formed from ·OH racial attack on atrazine forming DIA (*N*-dealkylation of the isopropylamino group) and subsequently forming DEDIA. This ·OH radical reaction mechanism involves H abstraction, which produces a carbon-centered radical. Each bond contains two electrons thus, breaking the neighbouring N-C bond will result in the formation of an electron lone pair. One electron will quench the carbon-centered radical, while simultaneously forming a new radical on the N atom. Subsequently, this N radical can abstract a H atom from water, regenerating the ·OH radical and forming the free amino group.

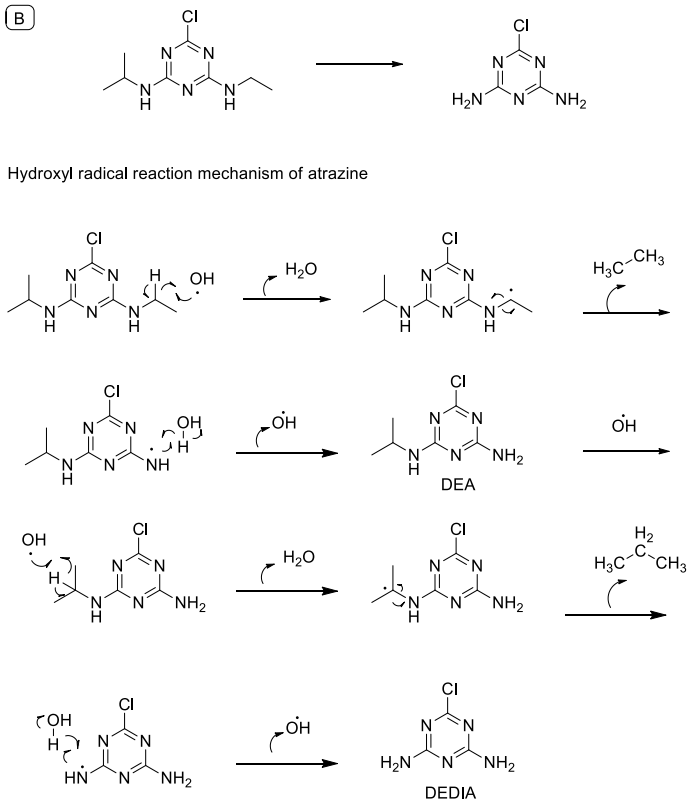


Fig. 22. Proposed mechanism for the formation of DEDIA through ·OH radical attack on atrazine

The formation of ATRA-Imine (Fig. 20.; B), through ·OH radical attack on atrazine during an AOP, was reported by Acero et al., (2000). In this study it was reported to be a primary DP but not a predominant DP. A mechanism for the formation of ATRA-imine through ·OH radical attack was also proposed. In this reaction mechanism a ·OH radical abstracts a H atom from the carbon (C) atom adjacent to N, producing a carbon-centered radical. Subsequently, the addition of O_2 to this intermediate results in the generation of a peroxide radical. Atrazine imine (ATRA-imine) is then formed following the loss of the perhydroxyl radical (Acero et al., 2000, Luo et al., 2017).

ATRA-imine is highly susceptible to hydrolysis which leads to the formation of the *N*-dealkylated derivative (DEA) (Acero et al., 2000). Since ATRA-imine is easily hydrolysed this may account for its absence in surface and natural waters (Luo et al., 2017). Therefore, ATRA-imine is not considered to be a persistent DP and a concern to the environment.

However, unlike ATRA-imine, DEDIA is resistant to chemical oxidation, including with very reactive species like ·OH radicals (Balci et al., 2009). Due to the persistent nature of DEDIA, Komtchou et al., (2017) highlighted that of all the atrazine DPs formed in that study, that DEDIA was the most important and significant DP.

Panshin et al., (2000), conducted an analysis of atrazine and four of its DPs in the pore water of the Vadose Zone, Central Indiana. After a single application of atrazine, atrazine DPs were identified in the following order: DEA > DEDIA > DIA. The following season, when atrazine was not applied, the concentrations of the atrazine DPs were identified in the following order: DEDIA > DEA > DIA. This observed change in the DP order is due to the degradation of DIA and DEA to DEDIA. However, the fact that DEDIA was the most abundant DP detected the following year, taking into account that atrazine was not applied onto crops, demonstrates its persistent and recalcitrant nature in the environment (Panshin et al., 2000). Furthermore, this study discussed that atrazine and its DPs move rapidly through soil. In particular this was discussed to be the case for DEDIA, as it has the lowest adsorption coefficient, making it more mobile than other atrazine DPs. Due to DEDIA's mobility and persistence in the environment, there could be a risk for it to persist in the environment and eventually contaminate drinking water supplies.

There are limited studies on the toxicity of DEDIA and ATRA-imine. However, DEDIA has been shown to demonstrate some toxicity. This included a recent study where DEDIA was evaluated for developmental effects in rabbits and rats (Scialli et al., 2014). This study reported that DEDIA was responsible for the reductions in fetal body weights of rats. However, despite the limited knowledge of the toxicity of DEDIA and ATRA-imine, the US-EPA have evaluated and categorized the triazine herbicides, including atrazine, and their most common chlorinated DPs, as having a common mechanism of toxicity (USEPA, 2003).

5.2. Pirimicarb Degradation Products

The pirimicarb DP was tentatively identified as 2-methylamino-5,6-dimethylpyrimidin-4-yl-dimethylcarbamate or desmethylpirimicarb (DMP). The DP of pirimicarb with its corresponding *m/z* ratio and RT is shown in Fig. 23.

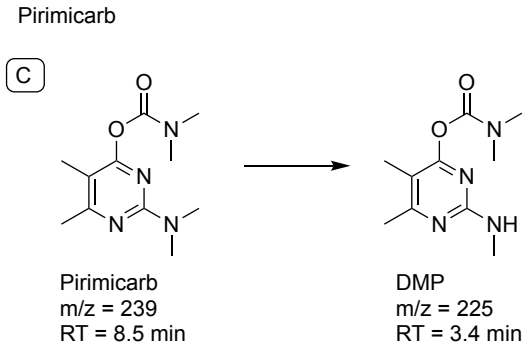


Fig. 23. Molecular structures of the proposed pirimicarb DP with the corresponding *m/z* ratio and RT

Table 16. shows the relative amounts of formation of DMP in the three pirimicarb ERG experiments. In T1 and T3, DMP was detected after 1 h. There was a steady increase in the formation of DMP until 36 h, after which there was a sharp decline in the amount of DMP detected/formed. In T2 DMP was detected after 3 h and throughout the time of the trial lower amounts of DMP were formed. Unlike T1 and T3, in T2 there was no sharp decline in the formation of DMP after 48 h.

Table 16. Formation of pirimicarb degradation product (DMP) and the corresponding recorded voltage values.

	Trial 1.		Trial 2.		Trial 3.	
Time (h)	DMP	Voltage	DMP	Voltage	DMP	Voltage
0	0	-	0	-	0	-
0.08	0	8.9	0	4.0	0	8.8
1	41	9.2	0	3.5	80	8.2
2	77	8.7	0	3.6	127	7.9
3	93	8.9	43	3.9	141	7.6
4	165	8.0	55	4.1	187	7.3
5	206	8.1	66	4.3	210	7.0
6	231	7.8	59	4.7	213	7.4
7	232	7.5	64	5.1	255	6.6
8	254	7.3	72	5.0	258	6.9
24	405	6.6	113	4.8	257	6.5
36	335	6.5	91	4.5	292	6.3
48	55	6.2	74	4.2	139	5.4
56	-	-	89	4.1	154	5.6
72	-	-	87	4.1	112	5.7
80	-	-	79	4.2	120	5.8

Values are expressed as response x 10^{-3}, where response is defined as peak area count of the metabolite/peak area count of the internal standard. The voltage was measured in volts.

Several research groups have reported on the formation of DMP as a DP of pirimicarb (Chen et al., 2009, Fenoll et al., 2015, Wu et al., 2016). Fenoll et al., (2015) identified DMP as a pirimicarb DP produced from the photocatalytic oxidation of pirimicarb in aqueous slurries containing a TiO_2 catalyst. The photocatalytic process initiates a series of chemical reactions that will eventually mineralise organic compounds, including through the formation and attack of ·OH radicals. In this study, the authors report that DMP was the second most abundant DP formed in the mineralisation of pirimicarb.

The formation of DMP through photocatalysis was also demonstrated by Wu et al., (2016). In this study they highlighted that ·OH radicals were the main active species involved in the degradation of pirimicarb. Similarly to Fenoll et al., (2015), they report that a major degradation pathway for the mineralisation of pirimicarb is through *N*-dealkylation. Wu et al., (2016) described the formation of DMP through the *N*-dealkylation of the 2-dimethylamino group of pirimicarb by ·OH radicals. They explain that C-H bonds adjacent to N atoms have a stereo- electronic effect and that that accounts for the high rates of H atom abstraction by electrophilic ·OH radicals. For this reason, H atoms in the 2-

dimethylamino group in the pirimicarb molecule are susceptible to a radical attack (Wu et al., 2016). The ·OH radical reaction mechanism itself involves H abstraction from the *N*-methyl group, resulting in the formation of water and a radical on the C adjacent to the N atom. This carbon-centered radical reacts rapidly with O_2 and transforms into an alkoxy radical. The fragmentation of this alkoxy radical produces the *N*-*N*-methylamino group (Lee and Choi, 2004).

The environmental fate of pirimicarb and its DPs have been investigated (Cabras et al., 1990, Taboada et al., 1994, Romero et al., 1994, Chen et al., 2009). Once released into the environment pirimicarb's DPs are susceptible to biotic and abiotic degradation. The main pathway for their bio- and photo-degradation include oxidative dealkylation and hydrolysis (Hill, 1978). Pirisi et al., (1969) studied the photo-degradation of pirimicarb including the corresponding photolysis rates and half-life of pirimicarb's DPs in water. They report that in water, DMP undergoes further degradation to the *N*-*N*-free amino (A) and the *N*-*N*-formylamino (B) derivative (Fig. 24). Subsequently, both DMP DPs were further photo-degraded to unknown species. They found that the associated environmental $t_{1/2}$ and $t_{1/100}$ values calculated for these DPs were suggestive that they have a relatively low risk of persistence in natural waters (Pirisi et al., 1996).

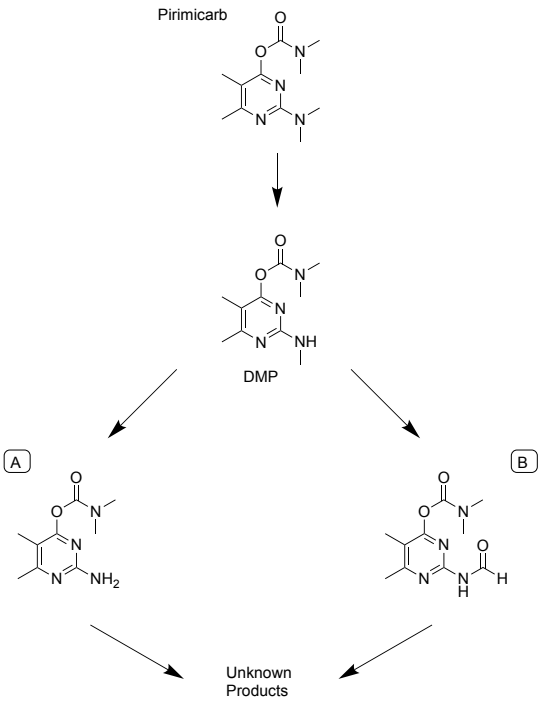


Fig. 24. Photo-degradation of pirimicarb in water (Pirisi et al., 1996)

Regarding the potential toxicity of DMP, pirimicarb only underwent a small alteration of a single structural moiety to form DMP. In this case, most of the parent's pesticide structure is still intact and

so it is possible that DMP will retain the same or a similar mode of action and toxicity as the parent compound (Parsons et al., 2008). As pirimicarb is reported to be acutely toxic towards mammals, due to its inhibition of the enzyme acetylcholinesterase (Machemer and Pickel, 1994), DMP may exhibit a similar effect.

Finally, it was observed that the increase in the formation of the DPs (Table 15. and 16.) mirrored the increase in the desorption of atrazine and pirimicarb (Table 11. and 12.). Furthermore, the formation of DPs decreases when the desorption of atrazine and pirimicarb decreases. This is an unusual observation, as the increase in the formation of DPs should correspond to a decrease in the adsorbate effluent concentration. This is an indication that the formation of the DPs could be occurring through in-direct oxidation and thus predominantly via ·OH radical attack. Direct oxidation of organic compounds can occur either through the diffusion of the adsorbate from the liquid phase to the anode surface or through oxidation of the adsorbate molecules on the anode surface (Anglada et al., 2009). In contrast, in in-direct oxidation, a strong oxidising agent (e.g.: ·OH) is electrochemically generated at the anode surface which destroys the adsorbate in the liquid phase (Fig. 25.).

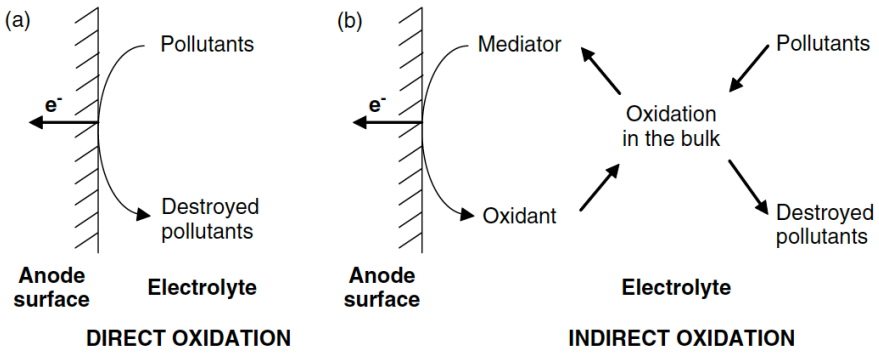


Fig. 25. Schemes for a) direct and b) indirect electrolytic treatment of pollutants (Anglada et al., 2009)

Thus, in order for in-direct electrochemical oxidation to occur, there must be adsorbate de-sorption from the Nyex bed in the electrolytic cell. In this study, adsorbate desorption was shown to occur during ERG of the Nyex. Thus, when the adsorbate molecules in the bed are desorbing into the liquid phase, they're being oxidised in the liquid by ·OH radicals, rather than being oxidised on the Nyex surface. As a result, there is a higher adsorbate concentration in the liquid phase and correspondingly a higher concentration of DPs formed through in-direct oxidation. Hence, an increase in the adsorbate effluent concentration was observed as well as an increase in the formation of DPs. Correspondingly, when the adsorbate liquid phase decreased (less desorption occurring), the amount of DPs formed,

also decreased. In-direct oxidation has been reported to play a key role in another study which investigated the formation of DPs during ERG of the Nyex (Hussain et al., 2013).

Chapter 4 – Conclusions and Future Work

1. Conclusion

In this study, the performance of the Nyex, for the removal of two trace level current-use pesticides, was evaluated. This was achieved through basic kinetic experiments, determining sorption isotherms and investigating the effects of an electrical current on their chemical behaviour and fate.

For atrazine and pirimicarb, a time of 2 h was determined to be sufficient for the Nyex to attain equilibrium conditions. Subsequently, adsorption isotherms and a range of different adsorption models provided an understanding of the mechanism of adsorption and the adsorptive performance of the Nyex. The single compound isotherm experiments demonstrated that there was a higher distribution of pirimicarb molecules, at equilibrium, adsorbed onto the Nyex, when compared to atrazine. This indicated a greater Nyex adsorption affinity toward the adsorption of pirimicarb. Nonetheless, the same mechanism of adsorption of both atrazine and pirimicarb was occurring and was best described as an L-shaped isotherm. The Freundlich Isotherm model was determined to be the optimal fit to the empirical data for atrazine and pirimicarb. This is consistent with the low surface area of the Nyex and its rough and heterogeneous surface morphology. The derived Freundlich parameters, *1/n* and K_f, were both high indicating that adsorption was favourable. The K_f value for pirimicarb was determined to be three times higher than the K_f value of atrazine. This indicated that the Nyex has a significantly higher adsorption capacity for pirimicarb.

Again, the Freundlich Isotherm was determined to fit the empirical data the best for atrazine and pirimicarb for the compound mixture isotherm experiments, which were conducted in raw water. Comparison of the Freundlich parameters from the single and mixed compound isotherms provided information of the effect the presence of both compounds and other NOM had on their adsorption. Lower *1/n* values indicated that the adsorption intensity was lower. Similarly, the derived K_f values were significantly lower, in particular for pirimicarb. This indicated that either the presence of an additional compound and/or the presence of NOM, reduced the Nyex's adsorption capacity for atrazine and pirimicarb. Thus, methods to try and reduce the amount of NOM before treatment or judicious placement of the unit, would greatly improve the adsorption of atrazine and pirimicarb onto the Nyex. The isotherm studies demonstrated that atrazine and pirimicarb were both suitable and

capable of being adsorbed onto the Nyex and may therefore be removed efficiently using a combined adsorption and electrochemical process.

Once the performance of the Nyex was established, the effectiveness of the ERG of the artificially pre-saturated Nyex was evaluated by passing a current through it. The results indicated that during ERG, atrazine and pirimicarb were transferred from the Nyex surface back into solution and detected in the effluent samples. This desorption was rationalised to stem from the modifications of the Nyex surface chemistry, changes in the localised pH around the Nyex, electro-desorption and the experimental method chosen to artificially pre-saturate the Nyex prior to ERG. The desorption was unexpected and time limitations restricted further work into investigating the cause of this effect. It is possible that artificial pre-saturation led to the desorption of both compounds and hence caused problems and interfered with the ERG of the Nyex. Thus, while in the present study ERG of the Nyex with *in-situ* electrochemical oxidation did not effectively treat or destroy atrazine and pirimicarb, this only indicates that further work needs to be done to improve and review the methodology to achieve the desired result.

Some treatment during ERG was observed, evidenced by the formation of DPs. Two atrazine DPs were formed and tentatively identified as ATRA-imine and DEDIA. While, one pirimicarb DP was formed and tentatively identified as DMP. DEDIA has a low reactivity towards ·OH radicals and is a DP of concern to the environment due to its recalcitrant nature. Unlike DEDIA, ATRA-imine is highly susceptible to hydrolysis and thus is not considered to be a persistent DP and a concern to the environment. Likewise, DMP is susceptible to abiotic and biotic degradation and is not considered to be a persistent compound. Therefore, although DPs were formed the relative number of DPs was low and from the three formed, one represented being a possible concern to the environment. Finally, ·OH radicals are thought to be the main species involved in the breakdown of atrazine and pirimicarb during the ERG. This was rationalised as the high and low rates of DP formation mirrored the increasing and decreasing adsorbate concentrations in the effluent samples.

Therefore, in summary looking back on the initial aims of the project (Chapter 1, section 4.) we can state:

1. A robust and accurate analytical method for the detection and quantification of atrazine and pirimicarb was developed. In addition, this method was used to tentatively identify the DPs formed on ERG of the saturated Nyex.

2. Adsorption behaviour of the Nyex adsorbent was investigated and kinetic studies, adsorption isotherms and breakthrough curves were all used to characterise the nature of the Nyex sorbate interactions. Additionally, studies in a raw water were undertaken to model possible interferences and/or competing adsorption in a "real system".
3. The potential treatment of atrazine and pirimicarb during ERG using electrochemical oxidation was studied. Given the limitations experienced of the "artificial pre-saturation" method, electrochemical oxidation was found to be ineffective. However, review of the methodology for future experiments could prove promising.
4. The fate and behaviour of atrazine and pirimicarb during ERG was evaluated.
5. The DPs found were tentatively identified and their potential impact on the natural environment assessed.

Overall therefore, all the initial aims of the project laid out in Chapter 1 section 4. were successfully met.

2. Future Work

Future work is required to investigate whether the observed atrazine and pirimicarb desorption, during ERG, was a physical or electro-desorptive effect. Furthermore, future work should be carried out on the optimisation of the experimental method, specifically relating to the artificial pre-saturation of the Nyex.

1. Physical Desorption

- Desorption Isotherm

A desorption isotherm experiment would help to evaluate the adsorption-desorption behaviour occurring between the dissolved atrazine and pirimicarb and the Nyex. A desorption isotherm experiment follows the same method of an adsorption isotherm experiment, in which the solid-phase concentration (q_e) and liquid-phase concentration (C_e), at equilibrium, are measured. Then, the adsorbent is removed and added to an adsorbate-free liquid-phase. At desorption equilibrium, the solid-phase concentration and liquid-phase concentrations are measured. An isotherm results by repeating this procedure using different initial adsorbate concentrations (Ditoro and Horzempa, 1982).

- pH Effect

The pH could play a major role in the solubility of atrazine and pirimicarb, resulting in desorption from the Nyex surface and should be investigated. The pH may increase the solubility of both compounds through ionisation and thus, the resulting desorption may actually be a physical desorption rather than an electrochemical effect. In order to evaluate the effect pH has on the adsorption of both compounds, adsorption isotherm/kinetic experiments at different pH values should be conducted.

2. Electrochemical Desorption

An experiment could be done in which the trials were repeated without pre-saturating the Nyex first. i.e.: Simultaneously adsorbing and destroying. Thus, if the observed desorption is due to an electro-

desorption effect, then running the current whilst your adsorbing one should not observe an increase in the adsorbate effluent concentration.

3. Nyex Saturation

The ERG experiments should be repeated, whereby the Nyex is saturated by passing the adsorbate solution through the Nyex bed, located in the tubular unit, prior to turning on the current . Thus, the Nyex would not be artificially pre-saturated. This would help evaluate if artificially pre-saturating the Nyex was responsible for the desorption of atrazine and pirimicarb.

References

- ACERO, J. L., STEMMLER, K. & VON GUNTEN, U. 2000. Degradation kinetics of atrazine and its degradation products with ozone and OH radicals: A predictive tool for drinking water treatment. *Environmental Science & Technology,* 34**,** 591-597.

- ADEYEMI, A. 2017. *The Recovery of Microalgae Cells onto a Non-porous Adsorbent.* Doctor of Philosophy, University of Manchester.

- AGENCY, E. P. 2013. Atrazine Preliminary Work Plan. EPA.

- AKSU, Z. & GONEN, F. 2004. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochemistry,* 39**,** 599-613.

- ALAVANJA, M. C. R. & BONNER, M. R. 2012. OCCUPATIONAL PESTICIDE EXPOSURES AND CANCER RISK: A REVIEW. *Journal of Toxicology and Environmental Health-Part B-Critical Reviews,* 15**,** 238-263.

- ANGLADA, A., URTIAGA, A. & ORTIZ, I. 2009. Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications. *Journal of Chemical Technology and Biotechnology,* 84**,** 1747-1755.

- ASGHAR, H. M. A. 2011. *Development of Graphitic Adsorbents for Water Treatment Using Adsorption and Electrochemical Regeneration.* Doctor of Philosophy, The University of Manchester.

- ASGHAR, H. M. A., ROBERTS, E. P. L., HUSSAIN, S. N., CAMPEN, A. K. & BROWN, N. W. 2012. Wastewater treatment by adsorption with electrochemical regeneration using graphite-based adsorbents. *Journal of Applied Electrochemistry,* 42**,** 797-807.

- ATSDR. 2003. *Tox Guide for Atrazine* [Online]. Agency for Toxic Substances
- and Disease Registry United States Department of Health and Human Services. Available: https://www.atsdr.cdc.gov/toxguides/toxguide-153.pdf [Accessed].

- BAILEY, H. D., INFANTE-RIVARD, C., METAYER, C., CLAVEL, J., LIGHTFOOT, T., KAATSCH, P., ROMAN, E., MAGNANI, C., SPECTOR, L. G., PETRIDOU, E. T., MILNE, E., DOCKERTY, J. D., MILIGI, L., ARMSTRONG, B. K., RUDANT, J., FRITSCHI, L., SIMPSON, J., ZHANG, L. P., RONDELLI, R., BAKA, M., ORSI, L., MOSCHOVI, M., KANG, A. Y. & SCHUZ, J. 2015. Home pesticide exposures and risk of childhood leukemia: Findings from the childhood leukemia international consortium. *International Journal of Cancer,* 137**,** 2644-2663.

- BALCI, B., OTURAN, N., CHERRIER, R. & OTURAN, M. A. 2009. Degradation of atrazine in aqueous medium by electrocatalytically generated hydroxyl radicals. A kinetic and mechanistic study. *Water Research,* 43**,** 1924-1934.

- BARBOSA, M. O., MOREIRA, N. F. F., RIBEIRO, A. R., PEREIRA, M. F. R. & SILVA, A. M. T. 2016. Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. *Water Research,* 94**,** 257-279.

- BAUP, S., JAFFRE, C., WOLBERT, D. & LAPLANCHE, A. 2000. Adsorption of pesticides onto granular activated carbon: Determination of surface diffusivities using simple batch experiments. *Adsorption-Journal of the International Adsorption Society,* 6**,** 219-228.

- BENOTTI, M. J., TRENHOLM, R. A., VANDERFORD, B. J., HOLADY, J. C., STANFORD, B. D. & SNYDER, S. A. 2009. Pharmaceuticals and Endocrine Disrupting Compounds in US Drinking Water. *Environmental Science & Technology,* 43**,** 597-603.

- BORRAS, N., OLIVER, R., ARIAS, C. & BRILLAS, E. 2010. Degradation of Atrazine by Electrochemical Advanced Oxidation Processes Using a Boron-Doped Diamond Anode. *Journal of Physical Chemistry A,* 114**,** 6613-6621.

- BRACK, W., DULIO, V., ARING, GERSTRAND, M., ALLAN, I., ALTENBURGER, R., BRINKMANN, M., BUNKE, D., BURGESS, R. M., COUSINS, I., ESCHER, B. I., HERNANDEZ, F. J., HEWITT, L. M., HILSCHEROVA, K., HOLLENDER, J., HOLLERT, H., KASE, R., KLAUER, B., LINDIM, C., HERRAEZ, D. L., MIEGE, C., MUNTHE, J., O'TOOLE, S., POSTHUMA, L., RUDEL, H., SCHAFER, R. B., SENGL, M., SMEDES, F., VAN DE MEENT, D., VAN DEN BRINK, P. J., VAN GILS, J., VAN WEZEL, A. P., VETHAAK, A. D., VERMEIRSSEN, E., VON DER OHE, P. C. & VRANA, B. 2017. Towards the review of the European Union Water Framework Directive: Recommendations for more efficient assessment and management of chemical contamination in European surface water resources. *Science of the Total Environment,* 576**,** 720-737.

- BROUWER, M., KOEMAN, T., VAN DEN BRANDT, P. A., KROMHOUT, H., SCHOUTEN, L. J., PETERS, S., HUSS, A. & VERMEULEN, R. 2015. Occupational exposures and Parkinson's disease mortality in a prospective Dutch cohort. *Occupational and Environmental Medicine,* 72**,** 448-455.

- BROWN, N. W. & ROBERTS, E. P. L. 2007. Electrochemical pre-treatment of effluents containing chlorinated compounds using an adsorbent. *Journal of Applied Electrochemistry,* 37**,** 1329-1335.

- BROWN, N. W., ROBERTS, E. P. L., CHASIOTIS, A., CHERDRON, T. & SANGHRAJKA, N. 2004a. Atrazine removal using adsorption and electrochemical regeneration. *Water Research,* 38**,** 3067-3074.

- BROWN, N. W., ROBERTS, E. P. L., GARFORTH, A. A. & DRYFE, R. A. W. 2004b. Electrochemical regeneration of a carbon-based adsorbent loaded with crystal violet dye. *Electrochimica Acta,* 49**,** 3269-3281.

- BUTKOVSKYI, A., JEREMIASSE, A. W., LEAL, L. H., VAN DER ZANDE, T., RIJNAARTS, H. & ZEEMAN, G. 2014. Electrochemical Conversion of Micropollutants in Gray Water. *Environmental Science & Technology,* 48**,** 1893-1901.

- CABRAS, P., SPANEDDA, L., CABITZA, F., CUBEDDU, M., MARTINI, M. G. & BRANDOLINI, V. 1990. PIRIMICARB AND ITS METABOLITE RESIDUES IN LETTUCE - INFLUENCE OF CULTURAL ENVIRONMENT. *Journal of Agricultural and Food Chemistry,* 38**,** 879-882.

- CARABIAS-MARTINEZ, R., GARCIA-HERMIDA, U., RODRIGUEZ-GONZALO, E. & RUANO-MIGUEL, L. 2005. Behaviour of carbamate pesticides in gas chromatography and their determination with solid-phase extraction and solid-phase microextraction as preconcentration steps. *Journal of Separation Science,* 28**,** 2130-2138.

- CHEN, T. W., FU, F. F., CHEN, Z. X., LI, D. Z., ZHANG, L. & CHEN, G. N. 2009. Study on the photodegradation and microbiological degradation of pirimicarb insecticide by using liquid chromatography coupled with ion-trap mass spectrometry. *Journal of Chromatography A,* 1216**,** 3217-3222.

- COUGHLIN, R. W. 1968. Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. *In:* EZRA, F. S. (ed.). Environ. Sci. Technol. ,.

- COUPE, R. H. & BLOMQUIST, J. D. 2004. Water-soluble pesticides in finished water of community water supplies. *Journal American Water Works Association,* 96**,** 56-68.

- CZEPIRSKI, L., BALYS, M. R. & KOMOROWSKA-CZEPIRSKA, E. 2000. Some generalization of Langmuir adsorption isotherm. *Internet Journal of Chemistry,* 3**,** 15.

- DABROWSKI, A., PODKOSCIELNY, P., HUBICKI, Z. & BARCZAK, M. 2005. Adsorption of phenolic compounds by activated carbon - a critical review. *Chemosphere,* 58**,** 1049-1070.

- DAVIES, J. E. D. & JABEEN, N. 2003. The adsorption of herbicides and pesticides on clay minerals and soils. Part 2. Atrazine. *Journal of Inclusion Phenomena and Macrocyclic Chemistry,* 46**,** 57-64.

- DITORO, D. M. & HORZEMPA, L. M. 1982. REVERSIBLE AND RESISTANT COMPONENTS OF PCB ADSORPTION DESORPTION - ISOTHERMS. *Environmental Science & Technology,* 16**,** 594-602.

- ECETOC. *Freundlich Isotherms* [Online]. European centre for ecotoxicology and toxicology of chemicals. Available: http://www.ecetoc.org/report/measured-partitioning-property-data/adsorption-desorption-distribution-kd-and-organic-carbon-water-partition-koc-coefficients/freundlich-isotherms/ [Accessed].

- EPA, U. 1999. *Pesticides - Fact Sheet for Pirimicarb* [Online]. United States Environmental Protection Agency. Available: https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_PC-106101_17-Aug-99.pdf [Accessed].

- EPA, U. 2005. Cancer Assessment Document. Evaluation of the Carcinogenic Potential of Pirimicarb. Cancer Assessment Review Committee. Health Effects Division. Office of Pesticide Programs. United States Environmental Protection Agency.

- EUROPEAN-COMMISSION. March, 2016. *Future Brief: Identifying Emerging risks for environmental policies* [Online]. European Commission. Available: http://ec.europa.eu/environment/integration/research/newsalert/pdf/emerging_environmental_risks_early_warnings_FB12_en.pdf [Accessed].

- FENOLL, J., GARRIDO, I., HEILIN, P., FLORES, P., VELA, N. & NAVARRO, S. 2015. Photocatalytic oxidation of pirimicarb in aqueous slurries containing binary and ternary oxides of zinc and titanium. *Journal of Photochemistry and Photobiology a-Chemistry,* 298**,** 24-32.

- FERA. Food and Environment Research Agency.

- FREUNDLICH, H. 1906. Uber Die Adsorption in Losungen. *Z. Phys. Chem*

- GEORGE, J. & SHUKLA, Y. 2011. Pesticides and cancer: Insights into toxicoproteomic-based findings. *Journal of Proteomics,* 74**,** 2713-2722.

- GHORAI, S. & PANT, K. K. 2005. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Separation and Purification Technology,* 42**,** 265-271.

- GILES, C. H., MACEWAN, T. H., NAKHWA, S. N. & SMITH, D. 1960. STUDIES IN ADSORPTION .11. A SYSTEM OF CLASSIFICATION OF SOLUTION ADSORPTION ISOTHERMS, AND ITS USE IN DIAGNOSIS OF ADSORPTION MECHANISMS AND IN MEASUREMENT OF SPECIFIC SURFACE AREAS OF SOLIDS. *Journal of the Chemical Society***,** 3973-3993.

- GOVERNMENT, A. 2016. *Atrazine Chemical Review* [Online]. Australian Pesticides and Veterinary Medicines Authority. Available: https://apvma.gov.au/node/12371 [Accessed].

- GUPTA, V. K., GUPTA, B., RASTOGI, A., AGARWAL, S. & NAYAK, A. 2011. Pesticides removal from waste water by activated carbon prepared from waste rubber tire. *Water Research,* 45**,** 4047-4055.

- HERNANDEZ, A. F., PARRON, T., TSATSAKIS, A. M., REQUENA, M., ALARCON, R. & LOPEZ-GUARNIDO, O. 2013. Toxic effects of pesticide mixtures at a molecular level: Their relevance to human health. *Toxicology,* 307**,** 136-145.

- HILL, I. R. 1978. *Microbial transformation of pesticides*, Acadamic Press, New York.

- HO, Y. S. & MCKAY, G. 1998. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection,* 76**,** 332-340.

- HU, J. Y., MARTIN, A., SHANG, R., SIEGERS, W., CORNELISSEN, E., HEIJMAN, B. & RIETVELD, L. 2014. Anionic exchange for NOM removal and the effects on micropollutant adsorption competition on activated carbon. *Separation and Purification Technology,* 129**,** 25-31.

- HUSSAIN, S. N. 2012. *Water Treatment Using Graphite Adsorbents With Electrochemical Regeneration.* Doctor of Philosophy, The University of Manchester.

- HUSSAIN, S. N., ROBERTS, E. P. L., ASGHAR, H. M. A., CAMPEN, A. K. & BROWN, N. W. 2013. Oxidation of phenol and the adsorption of breakdown products using a graphite adsorbent with electrochemical regeneration. *Electrochimica Acta,* 92**,** 20-30.

- HUSSAIN, S. N., TRZCINSKI, A. P., ASGHAR, H. M. A., SATTAR, H., BROWN, N. W. & ROBERTS, E. P. L. 2016. Disinfection performance of adsorption using graphite adsorbent coupled with electrochemical regeneration for various microorganisms present in water. *Journal of Industrial and Engineering Chemistry,* 44**,** 216-225.

- JAACKS, L. M. & STAIMEZ, L. R. 2015. Association of persistent organic pollutants and non-persistent pesticides with diabetes and diabetes-related health outcomes in Asia: A systematic review. *Environment International,* 76**,** 57-70.

- JAMES, K. A. & HALL, D. A. 2015. Groundwater Pesticide Levels and the Association With Parkinson Disease. *International Journal of Toxicology,* 34**,** 266-273.

- JESWANI, H. K., GUJBA, H., BROWN, N. W., ROBERTS, E. P. L. & AZAPAGIC, A. 2015. Removal of organic compounds from water: life cycle environmental impacts and economic costs of the Arvia process compared to granulated activated carbon. *Journal of Cleaner Production,* 89**,** 203-213.

- KIM, K. H., KABIR, E. & JAHAN, S. A. 2017. Exposure to pesticides and the associated human health effects. *Science of the Total Environment,* 575**,** 525-535.

- KIM, S. D., CHO, J., KIM, I. S., VANDERFORD, B. J. & SNYDER, S. A. 2007. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Research,* 41**,** 1013-1021.

- KOCK-SCHULMEYER, M., VILLAGRASA, M., DE ALDA, M. L., CESPEDES-SANCHEZ, R., VENTURA, F. & BARCELO, D. 2013. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. *Science of the Total Environment,* 458**,** 466-476.

- KOMTCHOU, S., DIRANY, A., DROGUI, P., DELEGAN, N., EL KHAKANI, M. A., ROBERT, D. & LAFRANCE, P. 2016. Degradation of atrazine in aqueous solution with electrophotocatalytic process using TiO2-x photoanode. *Chemosphere,* 157**,** 79-88.

- KOMTCHOU, S., DIRANY, A., DROGUI, P., ROBERT, D. & LAWRENCE, P. 2017. Removal of atrazine and its by-products from water using electrochemical advanced oxidation processes. Water Research.

- KUMAR, A. & XAGORARAKI, I. 2010. Pharmaceuticals, personal care products and endocrine-disrupting chemicals in U.S. surface and finished drinking waters: A proposed ranking system. *Science of the Total Environment,* 408**,** 5972-5989.

- LANGMUIR, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. ,.

- LAPWORTH, D. J., BARAN, N., STUART, M. E. & WARD, R. S. 2012. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. *Environmental Pollution,* 163**,** 287-303.

- LEDESMA, B., ROMAN, S., SABIO, E. & ALVAREZ-MURILLO, A. 2014. Aqueous thermal desorption as an effective way to regenerate spent activated carbons. *Journal of Supercritical Fluids,* 85**,** 24-30.

- LEE, J. S. & CHOI, W. Y. 2004. Effect of platinum deposits on TiO2 on the anoxic photocatalytic degradation pathways of alkylamines in water: Dealkylation and N-alkylation. *Environmental Science & Technology,* 38**,** 4026-4033.

- LERRO, C. C., KOUTROS, S., ANDREOTTI, G., FRIESEN, M. C., ALAVANJA, M. C., BLAIR, A., HOPPIN, J. A., SANDLER, D. P., LUBIN, J. H., MA, X. M., ZHANG, Y. W. & FREEMAN, L. E. B. 2015a. Organophosphate insecticide use and cancer incidence among spouses of pesticide applicators in the Agricultural Health Study. *Occupational and Environmental Medicine,* 72**,** 736-744.

- LERRO, C. C., KOUTROS, S., ANDREOTTI, G., HINES, C. J., BLAIR, A., LUBIN, J., MA, X. M., ZHANG, Y. W. & BEANE FREEMAN, L. E. 2015b. Use of acetochlor and cancer incidence in the Agricultural Health Study. *International Journal of Cancer,* 137**,** 1167-1175.

- LOOS, R., GAWLIK, B. M., LOCORO, G., RIMAVICIUTE, E., CONTINI, S. & BIDOGLIO, G. 2009. EU-wide survey of polar organic persistent pollutants in European river waters. *Environmental Pollution,* 157**,** 561-568.

- LUO, C. W., JIANG, J., GUAN, C. T., MA, J., PANG, S. Y., SONG, Y., YANG, Y., ZHANG, J. Q., WU, D. J. & GUAN, Y. H. 2017. Factors affecting formation of deethyl and deisopropyl products from atrazine degradation in UV/H2O2 and UV/PDS. *Rsc Advances,* 7**,** 29255-29262.

- LUO, Y. L., GUO, W. S., NGO, H. H., NGHIEM, L. D., HAI, F. I., ZHANG, J., LIANG, S. & WANG, X. C. C. 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment,* 473**,** 619-641.

- LUPUL, I., YPERMAN, J., CARLEER, R. & GRYGLEWICZ, G. 2015. Adsorption of atrazine on hemp stem-based activated carbons with different surface chemistry. *Adsorption-Journal of the International Adsorption Society,* 21**,** 489-498.

- MACHEMER, L. H. & PICKEL, M. 1994. CARBAMATE INSECTICIDES. *Toxicology,* 91**,** 29-36.

- MALATO, S., BLANCO, J., CACERES, J., FERNANDEZ-ALBA, A. R., AGUERA, A. & RODRIGUEZ, A. 2002. Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO2 using solar energy. *Catalysis Today,* 76**,** 209-220.

- MARTIN-GULLON, I. & FONT, R. 2001. Dynamic pesticide removal with activated carbon fibers. *Water Research,* 35**,** 516-520.

- MATTSON, J. S., MARK, H. B., MALBIN, M. D., WEBER, W. J. & CRITTEND.JC 1969. SURFACE CHEMISTRY OF ACTIVE CARBON - SPECIFIC ADSORPTION OF PHENOLS. *Journal of Colloid and Interface Science,* 31**,** 116-&.

- MEHTA, M. P. & FLORA, J. R. V. 1997. Effects of electrochemical treatment of granular activated carbon on surface acid groups and the adsorptive capacity for phenol. *Water Research,* 31**,** 2171-2176.

- MELO, L. F. C., COLLINS, C. H. & JARDIM, I. 2005. High-performance liquid chromatographic determination of pesticides in tomatoes using laboratory-made NH2 and C-18 solid-phase extraction materials. *Journal of Chromatography A,* 1073**,** 75-81.

- MORENO-CASTILLA, C. 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon,* 42**,** 83-94.

- MOSCHET, C., WITTMER, I., SIMOVIC, J., JUNGHANS, M., PIAZZOLI, A., SINGER, H., STAMM, C., LEU, C. & HOLLENDER, J. 2014. How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality. *Environmental Science & Technology,* 48**,** 5423-5432.

- MOSTAFALOU, S. & ABDOLLAHI, M. 2013. Pesticides and human chronic diseases: Evidences, mechanisms, and perspectives. *Toxicology and Applied Pharmacology,* 268**,** 157-177.

- MOUSSAVI, G., HOSSEINI, H. & ALAHABADI, A. 2013. The investigation of diazinon pesticide removal from contaminated water by adsorption onto NH4Cl-induced activated carbon. *Chemical Engineering Journal,* 214**,** 172-179.

- NABEERASOOL, M. A., CAMPEN, A. K., POLYA, D. A., BROWN, N. W. & VAN DONGEN, B. E. 2015. Removal of Metaldehyde from Water Using a Novel Coupled Adsorption and Electrochemical Destruction Technique. *Water,* 7**,** 3057-3071.

- NAM, S. W., CHOI, D. J., KIM, S. K., HER, N. & ZOH, K. D. 2014. Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. *Journal of Hazardous Materials,* 270**,** 144-152.

- NARBAITZ, R. M. & KARIMI-JASHNI, A. 2009. Electrochemical regeneration of granular activated carbons loaded with phenol and natural organic matter. *Environmental Technology,* 30**,** 27-36.

- NKRUMAH-AMOAKO, K., ROBERTS, E. P. L., BROWN, N. W. & HOLMES, S. M. 2014. The effects of anodic treatment on the surface chemistry of a Graphite Intercalation Compound. *Electrochimica Acta,* 135**,** 568-577.

- OLIVEIRA, R. C., JOUANNIN, C., GUIBAL, E. & GARCIA, O. 2011. Samarium(III) and praseodymium(III) biosorption on Sargassum sp.: Batch study. *Process Biochemistry,* 46**,** 736-744.

- PADHYE, L. P., YAO, H., KUNG'U, F. T. & HUANG, C. H. 2014. Year-long evaluation on the occurrence and fate of pharmaceuticals, personal care products, and endocrine disrupting chemicals in an urban drinking water treatment plant. *Water Res,* 51**,** 266-76.

- PAL, A., GIN, K. Y. H., LIN, A. Y. C. & REINHARD, M. 2010. Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. *Science of the Total Environment,* 408**,** 6062-6069.

- PANSHIN, S. Y., CARTER, D. S. & BAYLESS, E. R. 2000. Analysis of atrazine and four degradation products in the pore water of the vadose zone, central Indiana. *Environmental Science & Technology,* 34**,** 2131-2137.

- PARRON, T., REQUENA, M., HERNANDEZ, A. F. & ALARCON, R. 2014. Environmental exposure to pesticides and cancer risk in multiple human organ systems. *Toxicology Letters,* 230**,** 157-165.

- PARSONS, S., BOXALL, A., SINCLAIR, C. & RAMWELL, C. 2008. *Pesticide Degradates of Concern to the Drinking Water Community* [Online]. American Water Works Association. Available: http://www.waterrf.org/PublicReportLibrary/2938.pdf [Accessed].

- PEREZ, M. H., PENUELA, G., MALDONADO, M. I., MALATO, O., FERNANDEZ-IBANEZ, P., OLLER, I., GERNJAK, W. & MALATO, S. 2006. Degradation of pesticides in water using solar advanced oxidation processes. *Applied Catalysis B-Environmental,* 64**,** 272-281.

- PINTO, G. M. F. & JARDIM, I. 2000. Use of solid-phase extraction and high-performance liquid chromatography for the determination of triazine residues in water: validation of the method. *Journal of Chromatography A,* 869**,** 463-469.

- PIRISI, F. M., CABRAS, P., GARAU, V. L., MELIS, M. & SECCHI, E. 1996. Photodegradation of pesticides. Photolysis rates and half-life of pirimicarb and its metabolites in reactions in water and in solid phase. *Journal of Agricultural and Food Chemistry,* 44**,** 2417-2422.

- PROVOST, D., CANTAGREL, A., LEBAILLY, P., JAFFRE, A., LOYANT, V., LOISEAU, H., VITAL, A., BROCHARD, P. & BALDI, I. 2007. Brain tumours and exposure to pesticides: a case-control study in southwestern France. *Occupational and Environmental Medicine,* 64**,** 509-514.

- RADJENOUIC, J., BAGASTYO, A., ROZENDAL, R. A., MU, Y., KELLER, J. & RABAEY, K. 2011. Electrochemical oxidation of trace organic contaminants in reverse osmosis concentrate using RuO2/IrO2-coated titanium anodes. *Water Research,* 45**,** 1579-1586.

- RIBEIRO, A. R., NUNES, O. C., PEREIRA, M. F. R. & SILVA, A. M. T. 2015. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environment International,* 75**,** 33-51.

- RIVERO, J., LUZARDO, O. P., HENRIQUEZ-HERNANDEZ, L. A., MACHIN, R. P., PESTANO, J., ZUMBADO, M., BOADA, L. D., CAMACHO, M. & VALERON, P. F. 2015. In vitro evaluation of oestrogenic/androgenic activity of the serum organochlorine pesticide mixtures previously described in a breast cancer case-control study. *Science of the Total Environment,* 537**,** 197-202.

- ROMERO, E., SCHMITT, P. & MANSOUR, M. 1994. PHOTOLYSIS OF PIRIMICARB IN WATER UNDER NATURAL AND SIMULATED SUNLIGHT CONDITIONS. *Pesticide Science,* 41**,** 21-26.

- SAMANIC, C. M., DE ROOS, A. J., STEWART, P. A., RAJARAMAN, P., WATERS, M. A. & INSKIP, P. D. 2008. Occupational exposure to pesticides and risk of adult brain tumors. *American Journal of Epidemiology,* 167**,** 976-985.

- SANCHES, S., CRESPO, M. T. B. & PEREIRA, V. J. 2010. Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes. *Water Research,* 44**,** 1809-1818.

- SCHWAB, B. W., HAYES, E. P., FIORI, J. M., MASTROCCO, F. J., RODEN, N. M., CRAGIN, D., MEYERHOFF, R. D., D'ACO, V. J. & ANDERSON, P. D. 2005. Human pharmaceuticals in US surface waters: A human health risk assessment. *Regulatory Toxicology and Pharmacology,* 42**,** 296-312.

- SCHWARZENBACH, R. P., ESCHER, B. I., FENNER, K., HOFSTETTER, T. B., JOHNSON, C. A., VON GUNTEN, U. & WEHRLI, B. 2006. The challenge of micropollutants in aquatic systems. *Science,* 313**,** 1072-1077.

- SCIALLI, A. R., DESESSO, J. M. & BRECKENRIDGE, C. B. 2014. Developmental Toxicity Studies with Atrazine and its Major Metabolites in Rats and Rabbits. *Birth Defects Research Part B-Developmental and Reproductive Toxicology,* 101**,** 199-214.

- SHARMA, S. & BHATTACHARYA, A. 2017. Drinking water contamination and treatment techniques. Appl Water Sci.

- SHAUKAT, U., ISMAIL, M. & MEHMOOD, N. 2013. Epidemiology, Major Risk Factors and Genetic Predisposition for Breast Cancer in the Pakistani Population. *Asian Pacific Journal of Cancer Prevention,* 14**,** 5625-5629.

- SIMON PARSONS, A. B., CHRIS SINCLAIR , AND CARMEL RAMWELL. 2008. *Pesticide Degradates of Concern to the Drinking Water Community* [Online]. American Water Works Association. Available: http://www.waterrf.org/PublicReportLibrary/2938.pdf [Accessed].

- SMITH, E. H. & WEBER, W. J. 1989. EVALUATION OF MASS-TRANSFER PARAMETERS FOR ADSORPTION OF ORGANIC-COMPOUNDS FROM COMPLEX ORGANIC MATRICES. *Environmental Science & Technology,* 23**,** 713-722.

- SNYDER, S. A. 2008. Occurrence, treatment, and toxicological relevance of EDCs and pharmaceuticals in water. *Ozone-Science & Engineering,* 30**,** 65-69.

- TABOADA, E. R., DEKKER, A., VANKAMMENPOLMAN, A., SMELT, J. H., BOESTEN, J. & LEISTRA, M. 1994. ADSORPTION, DEGRADATION AND LEACHING OF PIRIMICARB IN ORCHARD SOILS. *Science of the Total Environment,* 153**,** 253-260.

- UFZ, H. C. F. E. R.-. February 27, 2017. *New standards for better water quality in Europe* [Online]. ScienceDaily. Available: www.sciencedaily.com/releases/2017/02/170227100740.htm [Accessed].

- UNSWORTH, J. 2010. *History of Pesticide Use* [Online]. International Union of Pure and Applied Chemistry. Available: http://agrochemicals.iupac.org/index.php?option=com_sobi2&sobi2Task=sobi2Details&catid=3&sobi2Id=31 [Accessed].

- VAN DER BRUGGEN, B., VANDECASTEELE, C., VAN GESTEL, T., DOYEN, W. & LEYSEN, R. 2003. A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environmental Progress,* 22**,** 46-56.

- VAN MAELE-FABRY, G., LANTIN, A. C., HOET, P. & LISON, D. 2011. Residential exposure to pesticides and childhood leukaemia: A systematic review and meta-analysis. *Environment International,* 37**,** 280-291.

- WELHOUSE, G. J. & BLEAM, W. F. 1993. ATRAZINE HYDROGEN-BONDING POTENTIALS. *Environmental Science & Technology,* 27**,** 494-500.

- WESTERHOFF, P., YOON, Y., SNYDER, S. & WERT, E. 2005. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environmental Science & Technology,* 39**,** 6649-6663.

- WFD, E. 2006. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. European Environment Agency.

- WHITACRE, D. M. *Reviews of Environmental Contamination and Toxicology*, Springer.

- WU, Y. S., CHEN, C. C., HUANG, Y. C., LIN, W. Y., YEN, Y. T. & LU, C. S. 2016. Pirimicarb degradation by BiVO4 photocatalysis: Parameter and reaction pathway investigations. *Separation Science and Technology,* 51**,** 2284-2296.

- ZAVISKA, F., DROGUI, P., BLAIS, J. F., MERCIER, G. & LAFRANCE, P. 2011. Experimental design methodology applied to electrochemical oxidation of the herbicide atrazine using Ti/IrO2 and Ti/SnO2 circular anode electrodes. *Journal of Hazardous Materials,* 185**,** 1499-1507.

Appendices

1. HPLC/DAD

Arvia Technology had a pre-existing optimised method for the detection of atrazine. This same method also allowed for the detection of pirimicarb. Thus, both compounds fell with ease into an existing analytical method.

Representative chromatograms showing the wavelength and RTs of atrazine and pirimicarb are shown in Fig. 26. and Fig. 27.., respectively.

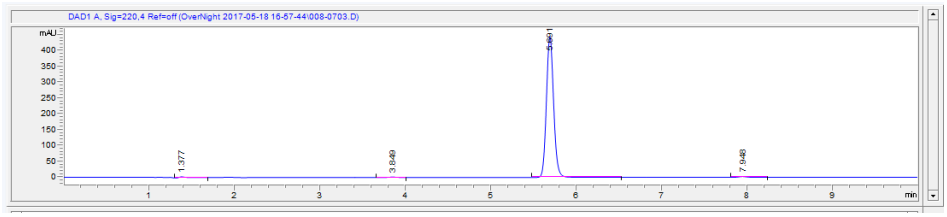


Fig. 26. representative chromatogram of atrazine, detection at wavelength 220 nm and a RT of 5.7 min

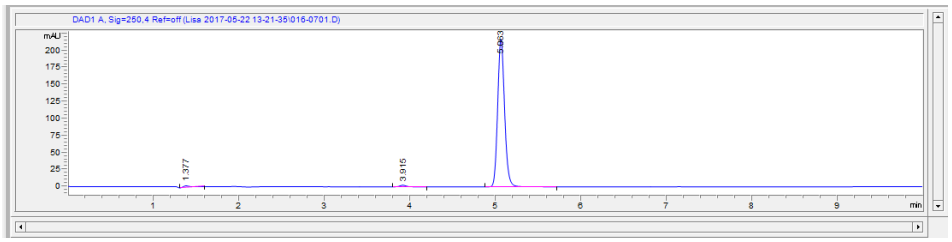


Fig. 27. representative chromatogram of pirimicarb, detection at wavelength 250 nm and a RT of 5.1 min

2. HPLC/MS Optimisation

The aim was to:

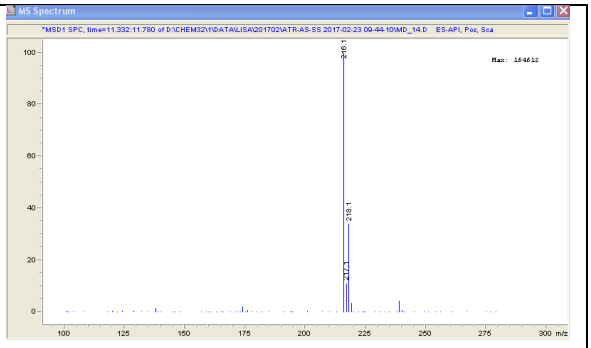
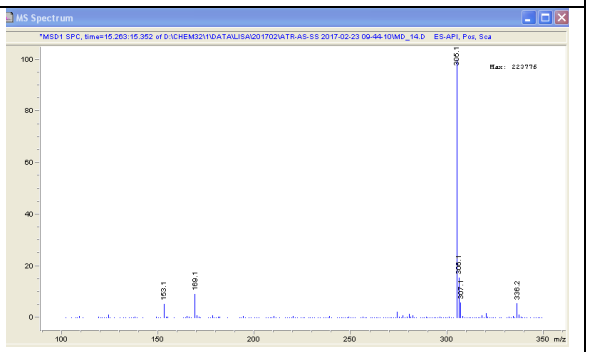
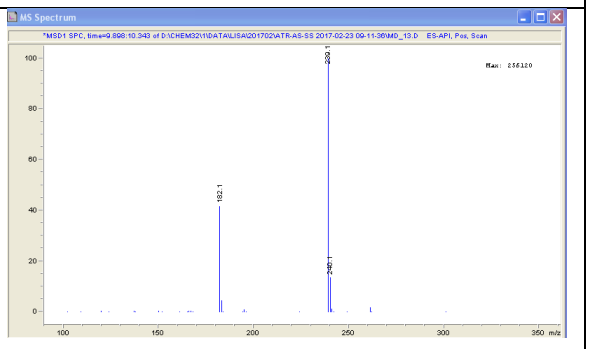
- Develop an optimised and robust HPLC/MS method for the identification and quantification of atrazine, diazinon, pirimicarb and simazine at ng/mL and pg/mL levels
- To develop an analytical method for the detection of any potential DPs

2.1 Development and Optimisation of the MS Detector Method

The aim was to:

- Identify suitable quantification and confirmation ions for each compound
- Subsequently to try to optimise MS parameters (e.g. fragmentor voltages) to achieve a high detection sensitivity for the analytes of interest

To obtain mass spectra, individual compound standards containing atrazine, diazinon, pirimicarb and simazine (1000 ng/mL) were injected straight onto the MS, without the use of a column in positive ionisation mode . The mass spectrum shows the abundance of ions formed depending on their *m/z* ratio. The highest signal was chosen as the quantification ion (QI). One or two more relatively high signals was used as confirmation ions (CI) (Fig. 26). Having the QI and CI ions for each target analyte the MS parameters were now optimised. In order to optimise the sensitivity of the MS, different fragmentor voltages (FV) were tested for each analyte. The optimal FVs for each analyte are shown below including their corresponding QI and CIs.

Mass spectrum of atrazine QI: 216.1, FV: 90 CI: 218.1, FV: 90	
Mass spectrum of diazinon QI: 305.1, FV: 130 CI: 169.1, FV: 180	
Mass spectrum of pirimicarb QI: 239.1, FV: 90 CI: 182.1, FV: 150	

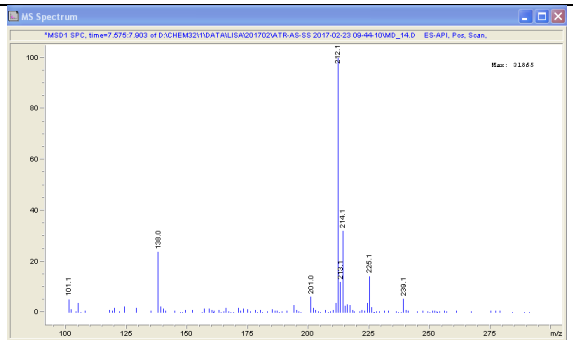
Mass spectrum of simazine QI: 212.1, FV: 60 CI: 214.1, FV: 60	

Fig. 28. Mass spectrum of atrazine, diazinon, pirimicarb and simazine including the quantification ion (QI), confirmation ion (CI) and fragmentor voltages (FV)

2.2 Development and Optimisation of the HPLC Method

The goal was to produce a mobile phase gradient programme that would:

- Achieve baseline separation of the target analytes (resolved peaks)
- Good chromatographic performance (slim, sharp peak shape)
- Have a short run time
- Have the analytes elute early and not remain in the column for too long, as otherwise peaks will often become broad

Important to note is that the pumps and tubing on this HPLC system have a dead volume of ca. 0.9 mL. At a flow of 0.2 mL/min this means that a certain mobile phase ratio reaches the column (and hence the compounds injected) only ca. 4.5 min after the pumps changed to this ratio according to the mobile phase gradient method.

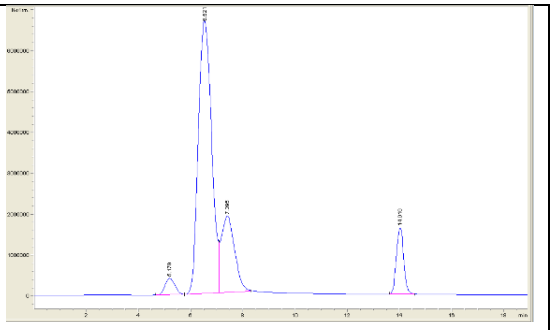
a) First the individual analytes (25 ng/mL) were injected onto the HPLC/MS to establish the elution order of these compounds. Solvent A: MQ water, solvent B: ACN

Elution order:
Simazine, pirimicarb, atrazine and diazinon

b) Then a standard containing all 4 analytes (25 ng/mL) was injected onto the HPLC/MS to try to optimise the mobile phase gradient. For all methods tested, solvent A: MQ water, solvent B: ACN and the flow rate was 0.2 mL/min.

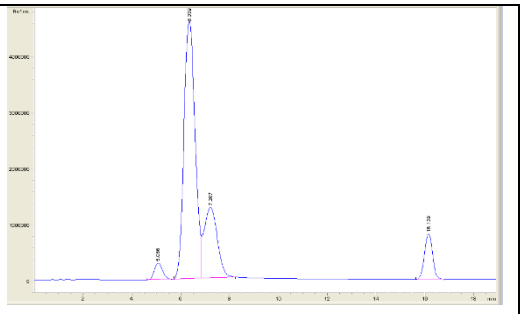
The first mobile phase gradient used was:

Time (min)	% B
0.00	40
9.00	80
11.00	80
12.00	40
19.00	40



Pirimicarb and atrazine are not resolved. This may be because of the sharp increase of the organic solvent (B) from 40 – 80 %, from 0 – 9 min. Therefore, the next step was to elongate the time it took for the mobile phase to reach 80 % B. This will decrease the mobile phase gradient slope from A to B. The reasoning being that the more aqueous mobile phase present in the column the more the analytes will be retained.

Time (min)	% B
0.00	40
15.00	80
17.00	80
18.00	40
22.00	40



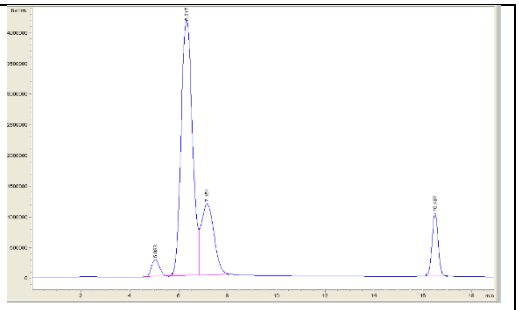
However, this did not improve the separation of these peaks.

The next approach was to have two steps in the increase of solvent B.

Step 1: 0 – 9 min, 40 – 60 % B (shallow gradient)

Step 2: 9 – 10 min, 60 – 80 % B (steep gradient)

As one of the aims is to keep the run time short you don't want to have a low % B run through the column for longer than necessary.

Time (min)	% B	
0.00	40	
09.00	60	
10.00	80	
12.00	80	
13.00	40	
19.00	40	

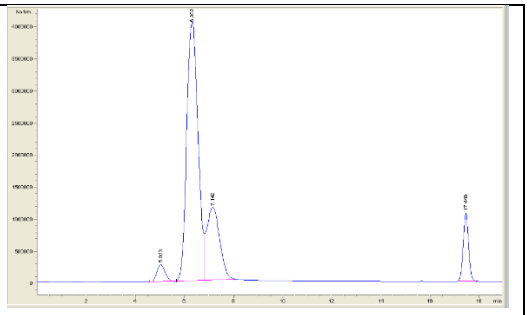
This did not help to resolve the peaks.

Subsequently having an even shallower mobile phase gradient slope in step 1 was tested.

I.e.: Step 1: 0 – 9 min, 40 – 50 % B

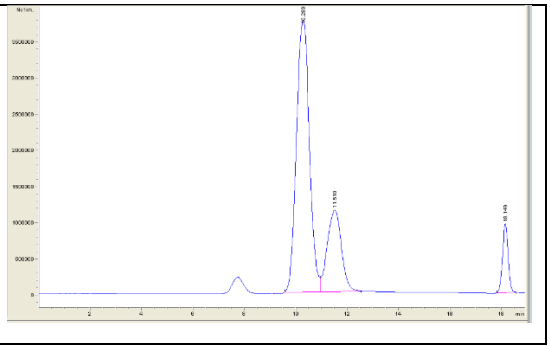
As well as a steeper mobile phase gradient in the second step.

I.e.: Step 2: 9 – 10 min, 50 – 80 % B

Time (min)	% B	
0.00	40	
09.00	50	
10.00	80	
12.00	80	
13.00	40	
19.00	40	

However, there was still no difference.

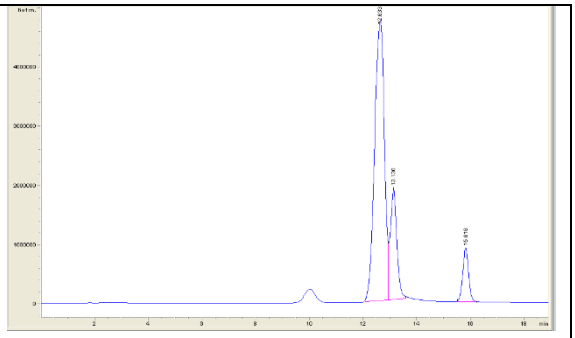
Therefore, we focused on the analytes at the entrance of the column. It is possible that an initial solvent ratio of 60:40 (A:B) is too high and causes pirimicarb and atrazine to co-elute.

Time (min)	% B	
0.00	30	
09.00	50	
10.00	80	
12.00	80	
13.00	30	
19.00	30	

There was a significant difference as pirimicarb and atrazine are almost resolved. It was noted that 6 min was not a long enough time for the pressure to stabilise to the initial starting mobile phase ratio and equilibrate the column.

Wanted to see what the chromatography would be like by decreasing the initial ratio, i.e.: 75:25. Also the time given to equilibrate the column was extended from 6 to 7 min.

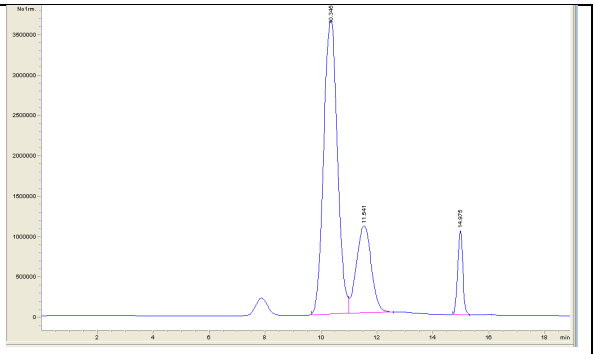
Time (min)	% B
0.00	25
06.00	45
07.00	80
11.00	80
12.00	25
19.00	25



This resulted in poor separation.

Subsequently, the following mobile phase gradient tested was as shown below. Here solvent B is increased to 90 % (instead of 80 %). The aim was to shorten the run time by having diazinon elute earlier. Having a high % of solvent B pass through the column would also elute any unwanted contaminants from the column. Again the time given for the column to re-equilibrate to the initial mobile phase ratio was 7 min.

Time (min)	% B
0.00	30
06.00	45
07.00	90
11.00	90
12.00	30
19.00	30

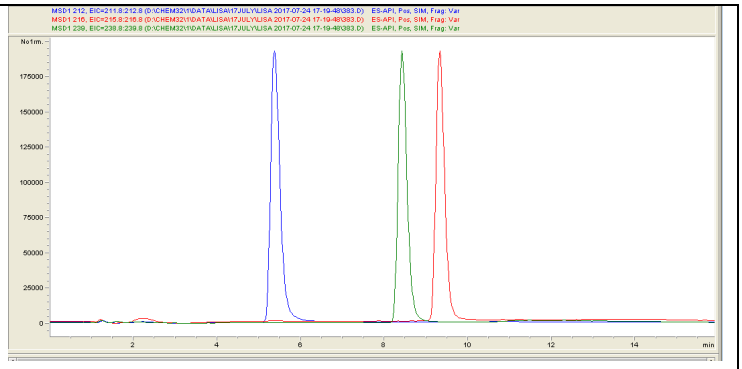


This method gave the best separation of pirimicarb and atrazine. Also, diazinon was eluted earlier (14.9 vs. 15.9 min) and the peak shape was slightly sharper and improved.

The method was slightly altered when Diazinon was no longer an analyte of interest in this study. Diazinon is the final compound to elute and the run could be shortened as it was no longer

necessary to have a high % of solvent B pass through the column for 4 min. From our previous method development we knew that the pump needed 7 min to allow the pressure to stabilise at the initial solvent ratio allowing the column to re-equilibrate. The final method run time was 16 min. This mobile phase gradient was used for all samples in Experiments III, IV and V is shown below. The RTs were as follows for simazine, pirimicarb and atrazine respectively: 5.4, 8.4 and 9.4 min.

Time (min)	% B
0.00	30
06.00	45
07.00	90
08.00	90
09.00	30
16.00	30



c) When doing the HPLC optimisation a 25 ng/mL standard was used, which produced nice peaks. However, on testing higher concentrations, i.e. 250 ng/mL, the chromatographic performance worsened considerably.

d) The column used until now had been used predominantly for environmental samples and was relatively old (Phenomenex Synergi 4u Fusion-RP 80 Å 150 x 2.00 mm 4-micron column). It was replaced with a newer column which had been used mostly for standards (Agilent Poroshell 120 EC-C18 2.1 x 100 mm 2.7 micron column). The same method was used on the new column to inject the higher concentrated standard. The chromatography remained poor.

e) The next approach was to investigate whether altering the solvent composition in the samples and standards would have an effect on the peak shape of the analytes. For the solvent composition investigation a mixed compound standard at 1000 ng/mL was used with varying solvent compositions. The first solvent composition tested was 50:50 MQ:ACN, this gave very poor chromatography. Then a ratio of 80:20 was tested, the chromatography was much improved and produced slim peaks. However, there was a slight split in the pirimicarb peak. To investigate if we could fix this slight split, a ratio of 85:15 was tested. This made no difference to the peak split or peak shape. A solvent composition ratio of 80:20 for all standards, QC samples and study samples was therefore chosen.

f) Although the chromatography and peak shape for the CS was very good from 1 – 1000 ng/mL at the beginning of the study the linear range for atrazine and pirimicarb was from 1 -250 ng/mL and for diazinon 1 – 10 ng/mL. However, over time the linearity deteriorated and a quadratic equation gave a better fit for atrazine.

g) The sensitivity of the method was evaluated by running CSs from 0.01 ng/mL (10 pg/mL). For atrazine and pirimicarb, the limit of detection (LOD) was 0.05 and 0.01 ng/mL, respectively and the signal/noise ratio was above 3.

2.3. Development of Analytical Method for the detection of Degradation Products

- The same MP gradient used for the identification and quantification of atrazine and pirimicarb in SIM mode was used for identification of the DPs in full-scan mode
- The *m/z* range chosen to scan for DPs was 70 - 250
- The default value of 90 was chosen for the fragmentor voltage
- The chosen extracted molecular ions were picked due to previous studies in which these ions were identified as atrazine and pirimicarb DPs

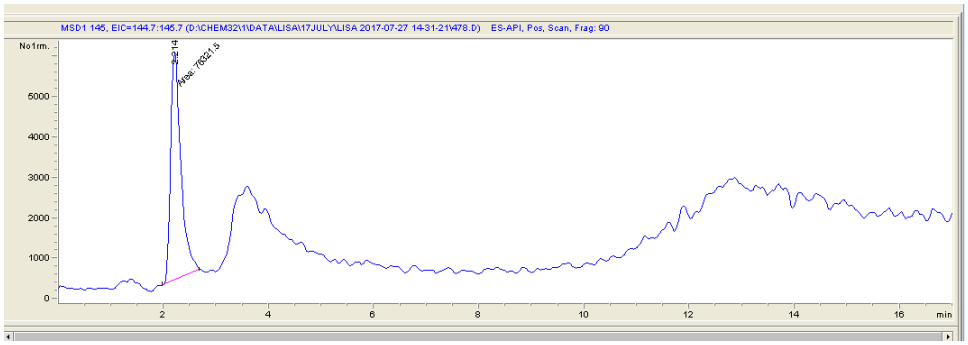
Degradation Product Chromatograms:

Atrazine

i. DEDIA

m/z: 145

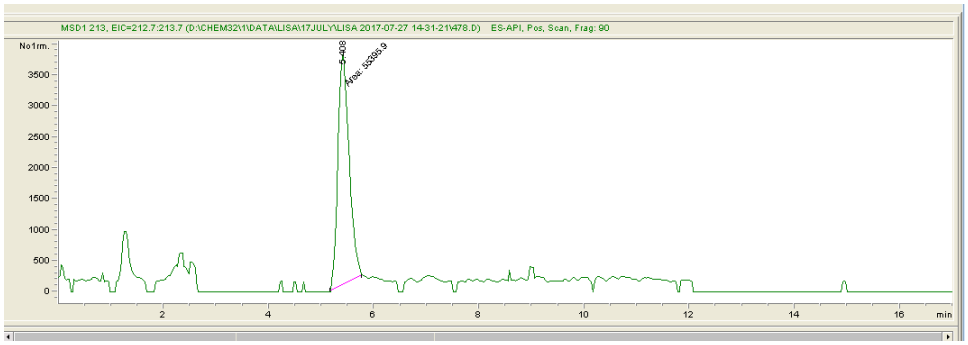
RT: 2.2 min



ii. ATRA-imine

m/z: 213

RT: 5.4 min



Pirimicarb

i. DMP

m/z: 225

RT: 3.4 min