The Removal of Chlorophenoxy Herbicides from Drinking Water by Activated Carbon Adsorption and Liquid Core Microcapsule Perstraction

Nora Engels

BSc. Chemical and Pharmaceutical Sciences
Student ID: 53306348

For the award of

Master of Science

to the

Dublin City University

Faculty of Science, School of Biotechnology

Supervisors: Prof. Marison, Dr. Tobin, Dr. Morrissey and Dr. Nolan

Submitted: January 2012

One volume

Declaration

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Abstract

Drinking water quality reports have highlighted a persistent trend in pesticide detection in the Republic of Ireland. One of the main concerns of the drinking water industry is that consistent pesticide removal rates do not occur despite the existence of activated carbon (AC) treatment regimes in most plants. The present work examines the removal of three chlorophenoxy herbicides (MCPA, 2,4-D and dichlorprop) from aqueous solutions by AC adsorption and a novel liquid-core microcapsule perstraction system. Herbicide adsorption to three ACs used in the drinking water industry was dependant on the pH of the water. As pH increased, adsorption decreased. Herbicide adsorption to AC was further decreased when humic acid (HA) was added to the contacting system. HA uptake by AC was minimal, possibly due to the large molecular weight associated with HA. Herbicide adsorption to AC was hindered by the presence of HA in the sample solutions and by HA pre-saturated to the AC. The possible interaction between herbicides and HA was investigated by UV-Visible and fluorescence spectroscopy to evaluate any potential interactions occurring during site competition. Weak spectral changes were observed and the florescence intensity was quenched by HA addition, suggesting that some form of interaction occurs. Capsular perstraction of MCPA, 2,4-D and dichlorprop by dibutyl sebacate liquid-core microcapsules (LCMs) was demonstrated. The use of LCMs results in between 9 and 18 % of the herbicides being extracted within 60 minutes of capsule addition. The quantity of LCMs added was equal to 1 g of oil core and could be increased to achieve higher levels of extraction. The results were compared to adsorption by 1 g of activated carbon (AquaSorb 2000) over the same time period of 100 minutes. Although the remediation of herbicides was more effective, AC equilibrium had not been reached after 100 minutes. The results demonstrate the time efficiency incurred by using LCMs compared to AC.

Acknowledgments:

Firstly, I would like to thank my parents, to whom I dedicate this thesis. Without you this process would not have been possible. Thank you for your continued support, wisdom and faith in me. A special thanks also to my wonderful brother and sister-in-law.

Thank you to my dear friends Sharon, Jamie, Nadia, Ross, Moira and Gavin for all the cups of tea and coffee and wonderful conversations throughout the years. Thank you to Sander for all your support. A special thank you to my friends in both labs and within the School, you know who you are.

I would like to thank Dr. Kieran Nolan for all the support, corrections and advice. You were a wonderful supervisor and I will always be grateful for that.

Thank you to the technical staff in DCU, Brian, Kashia and others.

Lastly, I would sincerely like to thank the Questor Centre in Belfast for this funding opportunity and this experience.

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Nomenclature

$\overline{x}$	Average
σ	standard deviation
ε	Molar absorptivity coefficient
C_e	Equilibrium herbicide concentration, mmol/L
C_i	Initial herbicide concentration, mmol/L
I	Fluorescence intensity in the presence of different quencher concentrations
I^0	Fluorescence intensity in the absence of a quencher
K_f	Parameter in the Freundlich equation, (mmol/g)(mmol/L)$^{-\frac{1}{n}}$
K_L	Parameter in the Langmuir equation, L/mmol
m	Number of observations in the experimental isotherm
p	Number of parameters in the regression model
q	Equilibrium amount of herbicide on the adsorbent, mmol/g
Q_i	Estimate from the isotherm for corresponding q_i
q_i	Observation from the batch experiment i
q_m	Maximum amount of herbicide per unit weight of adsorbent, mmol/g

R_L	Dimensionless parameter derived from the Langmuir equation
2,4-D	2,4-dichlorophenoxy acetic acid
4^a	Unbuffered solution adjusted to pH 4 with NaOH
4^b	Unbuffered solution with an initial pH value of 4
a	Front peak width
b	Back peak width
BHC	Benzene hexachloride
C_M	Measured concentration
C_m	Herbicide concentration in the microcapsule at time, t
C_m^0	Initial herbicide concentration in the microcapsule at time, t
C_m^e	Equilibrium herbicide concentration in the microcapsule at time, t
C_T	Theoretical concentration
C_{aq}	Herbicide concentration at time, t
C_{aq}^0	Initial herbicide concentration at time, t
C_{aq}^e	Equilibrium herbicide concentration in the aqueous phase at time, t
d_m	Diameter of the microcapsule
d_{lc}	Diameter of the liquid-core
DBS	Dibutyl sebacate
DDT	Dichlorodiphenyltrichloroethane
dichlorprop	2-(2,4-dichlorophenoxy) propionic acid
DWD	Drinking Water Directive

DWTP	Drinking water treatment plant
EPA	Environmental Protection Agency
FDA	United States Food and Drug Administration
ICH	International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use
IPM	Integrated Pest Management
ISO	International Organization for Standardization
K_{OC}	Soil sorption coefficient
K_{SV}	Stern-Volmer constant
k'	Capacity factor
LOD	Limit of detection
LOQ	Limit of Quantitation
MCPA	4-chloro-2-methylphenoxy acetic acid
MCPP	2-(4-chloro-2-methylphenoxy)propanoic acid
MOPS	3-(N-Morpholino) propanesulfonic acid
n	Parameter in the Freundlich equation
POP	Persistent Organic Pollutant
Q	Quencher
ROI	Republic of Ireland
RSD	Relative standard deviation
S	Slope of the calibration curve

SE	Standard error of estimates
SSE	Residual sum of squares
T	Tailing factor
t_0	Elution time of the void volume or non-retained components
t_R	Retention time of the analyte
U.S. EPA	United States Environmental Protection Agency
USP	United States Pharmacopoeia
V	Volume of solution, L
V_m	Volume of the microcapsules
V_{aq}	Volume of the aqueous phase
W	Weight of adsorbent, g
WHO	World Health Organisation

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Chapter 1

Introduction to pesticides, their application and detection in drinking water

1.1 Introduction

1.2 Pesticides

The term ”pesticide” is a broad term used to describe a substance or mixture of substances used to control pests. The full IUPAC definition for a pesticide is [1]:

> *Substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood, wood products or animal feedstuffs, or which may be administered to animals for the control of insects, mites/spider mites or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant, or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage or transport.*

This section will explore a number of topics associated with pesticides, beginning with a brief introduction into how pesticides have evolved throughout history. This is followed by an overview of how pesticides are classified and how they work, statistics on global usage and a review of how pesticides can have a negative impact on our health.

1.2.1 Historical background

The earliest form of pest control was in 2500 B.C. when the Sumarians used sulphur compounds to control insects and mites. In 1200 B.C. mercury and arsenical compounds were used in China to control body lice. Classical literary works examined by Smith and Secoy [2] showed how religion, folk magic and chemicals were used during ancient Greek and

Roman periods to control plant diseases, weeds and pests. The religious and folk magic practices includes prayers, sacrifices and rituals involving reptiles, herbs and remedies. Insects, rodents and other pests were eliminated with baits poisoned by arsenic, hemlock and amurca. Early insect repellents used citron, garlic, fig and ivy. Fumigation techniques were employed by boiling a mixture of amurca, bitumen and sulphur.

The use of pesticides evolved from these methods, becoming more focused on chemical methods. Smith and Secoy [3] reviewed the use of inorganic substances in Europe before 1850 to control pests, increase crop yields and tackle and prevent diseases. Sulphur was a popular pesticide because it showed insecticidal and fungicidal properties. Mercury, mercuric chloride, antimony and arsenical compounds were used to poison birds and vermin. Bittern, sodium chloride, iron and iron salts were used as herbicides. Insect populations were controlled by fumigation and spraying infected areas with sulphur, sulphuric acid, mercury, and calcium oxide (quicklime). Copper sulphate was used as an effective wood preservative against fungi. A popular method to decrease crop diseases was to add chemicals such as calcium hydroxide (lime), potassium nitrate (saltpeter), copper acetate, arsenic and hydrated potassium aluminium sulphate (alum) to seed steeps before germination. However, using arsenic for this purpose was banned in France in the late 1700s when high levels of arsenic were found in bread.

The methods described by Smith and Secoy [3] were the forerunners of modern day pesticides. Many of these methods were either too ineffective or too toxic. Pesticides were sought which could be engineered to be effective in smaller quantities, more target specific and be less persistent in the environment. Synthetic pesticides, meant to reach these criteria, were developed post World War II. Unlike the previous natural pesticides, these were synthetic organic compounds. The release of DDT (dichlorodiphenyltrichloroethane), BHC (benzene hexachloride), aldrin, dieldrin, endrin and 2,4-D revolutionised the agricultural industry. DDT was popular because it was inexpensive, easy to use, broad-spectrum, low mammalian toxicity and helped in the reduction of insect borne diseases like malaria, yellow fever and typhus. The first cases of insect resistance in houseflies to DDT were reported in 1946 and continued to be investigated throughout the 1950's and 1960's [4, 5, 6].

The 1962 publication of Rachel Carson's book Silent Spring [7] highlighted the environmental and toxicological effects caused by excessive pesticide application, including DDT. This was followed by a ban on DDT in 1972 by the EPA following concerns that DDT posed a carcinogenic risk on humans [8]. The 2001 Stockholm Convention on persistent organic pollutants (POPs) added a limited exemption on the use of DDT for indoor residual spraying in malaria zones [9]. This decision was backed by the World Health Organization (WHO) in 2006, which lists DDT as one of 12 recommended insecticides for this purpose [10].

1.2.2 Overview of pesticide characterisation and classification

Pesticides are generally classified based on three criteria: target pest controlled, chemical class and type of hazard. The main types of pesticides, according to the type of pest they control, are listed in Table 1.1. Each type of pesticide can be further subdivided into groups. For example, herbicides can be either chlorophenoxy compounds or bipyridyl derivatives. Pesticides are pest specific in their mode of action. Insecticides act on four nerve targets present in animals but not plants: the acetylcholine receptor, acetylcholinesterase, the voltage-gated chloride channel and the γ-aminobutyric acid receptor. Herbicides act on plant specific pathways such as photosynthesis, carotenoid synthesis, aromatic and branched chain amino acid synthesis essential in plants but not mammals. Fungicides block ergosterol or tubulin synthesis and cytochrome c reductase [11].

Chemical classes of pesticides are generally not referred to by their full chemical name but rather by an official common name assigned by the International Organization for Standardization (ISO) [12]. For example, the herbicide 2,4-dichlorophenoxy acetic acid is commonly known as 2,4-D. Pesticides may be classified according to their chemical structure. Chemical classes can be grouped as organic or inorganic and ionic and non-ionic. Ionic pesticides are further subdivided into cationic, basic and acidic groups. Non-ionic pesticides are further sub-divided by their significant physico-chemical properties like chlorinated, organophosphates and urea [13].

Table 1.1: Pesticide classification according to the type of pest controlled

Type	Type of pest controlled
Algicides	Control algae growth in water bodies such as lakes and swimming pools.
Antifouling agents	Kill or repel organisms that attach to underwater surfaces such as the hull of a boat.
Antimicrobials	Kill microorganisms.
Attractants	Attracts pests.
Biopesticides	Pesticides which are derived from a natural source.
Biocides	Kill microorganisms.
Defoliants	Causes leaves or other foliage to drop from a plant.
Desiccants	Promote drying of living tissue.
Disinfectants and sanitizers	Kill or inactivate microorganisms on inanimate objects.
Fungicides	Kill fungi.
Fumigants	Produce gas or vapor to kill pests in buildings or soil.
Herbicides	Kill unwanted weeds and other plants.
Insect growth regulators	Disrupts the life process of insects.
Insecticides	Kill insects and other arthropods.
Miticides	Kill mites feeding on plants and animals.
Microbial pesticides	Microorganisms that kill, inhibit or out compete pests.
Molluscicides	Kill snails and slugs.
Nematicides	Kill nematodes.
Ovicides	Kill eggs of insects and mites.
Pheromones	Disrupt the mating behaviour of insects.
Plant growth regulators	Alters the expected growth, flowering and reproduction of plants.
Repellents	Repel pests such as mosquitoes and flies.
Rodenticides	Control mice and other rodents.

WHO has established a classification system to distinguish between the more and the less hazardous forms of selected pesticides based on acute risk to human health by considering the toxicity of the technical active substance. The risk to human health is based on single or multiple exposures over a relatively short period of time. Pesticides are classified [14] as follows :

- Extremely hazardous (Class Ia) - e.g. parathion, aldicarb and calcium cyanide
- Highly hazardous (Class Ib) - e.g. carbofuran, mercuric oxide and warfarin
- Moderately hazardous (Class II) - e.g. chlorpyrifos, DDT and 2,4-D
- Slightly hazardous (Class III) - e.g. atrazine, diuron, glyphosate
- Unlikely to present acute hazard in normal use - e.g. bromacil, propazine and phosphorus acid

1.2.3 Global usage statistics

Pesticide use varies from year to year depending on weather, pest problems, economics and types of crops planted. The most recent statistics available on global and U.S. pesticide use were published by the U.S. Environmental Protection Agency (U.S. EPA) [15] in 2011. This report summarised the global and U.S. pesticide usage between 2006 and 2007. In the year 2007, world pesticide expenditure totalled more than $ 39.4 billion. Herbicides accounted for the biggest proportion of this expenditure (approximately 40 %). The U.S. expenditure on pesticides accounted for 32 % of the global market. The sectors using the pesticides are defined as follows:

- Agriculture
- Home and garden
- Industrial, commercial and government

Table 1.2: Most commonly used pesticide active ingredient, U.S. agricultural market sector 2007 estimates. Ranked by range in millions of pounds of active ingredient [15].

Active Ingredient	Type	Rank	Range
Glyphosate	Herbicide	1	180 - 185
Atrazine	Herbicide	2	73 - 78
Metam Sodium	Fumigant	3	50 - 55
Metolachlor-S	Herbicide	4	30 - 35
Acetochlor	Herbicide	5	28 - 33
Dichloropropene	Fumigant	6	27 - 32
2,4-D	Herbicide	7	25 - 29
Methyl Bromide	Fumigant	8	11 - 15
Chloropicrin	Fumigant	9	9 - 11
Pendimenthalin	Herbicide	10	7 - 9
Ethephon	Plant growth regulator	11	7 -9
Chlorothalonil	Fungicide	12	7 - 9
Metam Potassium	Fumigant	13	7 - 9
Chlorpyrifos	Insecticide	14	7 - 9
Copper Hydroxide	Fungicide	15	6 - 8
Simazine	Herbicide	16	5 - 7
Trifluralin	Herbicide	17	5 - 7
Propanil	Herbicide	18	4 - 6
Mancozeb	Fungicide	19	4 - 6
Aldicarb	Insecticide	20	3 - 4
Acephate	Insecticide	21	2 - 4
Diuron	Herbicide	22	2 - 4
MCPA	Herbicide	23	2 - 4
Paraquat	Herbicide	24	2 - 4
Dimethenamid	Herbicide	25	2 - 4

Table 1.2 shows the top 25 ranked pesticides in the U.S. agricultural market sector in 2007. Glyphosate (a herbicide) was the most commonly used active ingredient, followed by atrazine. It is important to note that the sale and use of atrazine was banned by the European Commission in 2004 because of concerns over groundwater contamination [16] but it remains the second most popular agricultural herbicide in the U.S.

Tables 1.3 and 1.4 show the top 5 ranked pesticides used in the U.S. home and garden sector and the U.S. industrial, commercial and government sector in 2007. The herbicide 2,4-D is the most widely used in both sectors.

Table 1.3: Most commonly used pesticide active ingredient, U.S. home and garden market sector 2007 estimates. Ranked by range in millions of pounds of active ingredient [15].

Active Ingredient	Type	Rank	Range
2,4-D	Herbicide	1	8 - 11
Glyphosate	Herbicide	2	5 - 8
Carbaryl	Insecticide	3	4 - 6
MCPP	Herbicide	4	4 - 6
Pendimethalin	Herbicide	5	3 - 5
Pyrethroids	Inseecticide	6	2 - 4
Malathion	Insecticide	7	2 - 4
Dicamba	Herbicide	8	1 - 3
Trifluralin	Herbicide	9	1 - 3
Pelarganoc Acid	Herbicide	10	<1

Table 1.4: Most commonly used pesticide active ingredient, U.S. Industry/Commercial/Government market sector 2007 estimates. Ranked by range in millions of pounds of active ingredient [15].

Active Ingredient	Type	Rank	Range
2,4-D	Herbicide	1	19 - 22
Glyphosate	Herbicide	2	13 - 15
Chlorothalonil	Fungicide	3	3 - 5
MSMA	Herbicide	4	2 - 4
Diuron	Herbicide	5	2 - 4
Pendimethalin	Herbicide	6	2 - 4
Triclopyr	Herbicide	7	2 - 4
Copper Sulfate	Fungicide	8	2 - 4
Malathion	Insecticide	9	1 - 3
Sulfuryl Fluoride	Insecticide	10	1 - 3

Although fluctuations in data from year to year occur, the user expenditure for pesticide use in the U.S. has increased since 1988 [15, 17, 18, 19, 20]. However, the quantity of pesticide active ingredients used has decreased since their peak in 1979 (1,144 millions of pounds) to 857 millions of pounds in 2007 [15]. The downwards trend in active ingredient quantities can be attributed to a combination of selective and effective pesticides, pest management initiatives and environmental awareness.

1.2.4 Effect on health

WHO estimates that approximately 3 million cases of pesticide poisoning occur annually, of which in excess of 250,000 result in death. These figures represent a mixture of intentional and unintentional poisonings. Agricultural communities in low to middle income countries such as China, India, Sri Lanka and Vietnam have a serious problem of self-harm by intentional pesticide poisoning. WHO figures show that pesticide ingestion accounts for 30 % of self-harm methods for India (1990), 71 % in Sri Lanka (1980-89) and 62 % in China (1998-2000) [21].

Unintentional poisoning and repeat exposure to pesticides can occur in a number of ways. Pesticide handlers risk exposure to pesticides through ingestion, inhalation and skin contact during the mixing and application process [22]. People in residential proximity to sites where pesticides are used [23] may be exposed by pesticide drift.

Once absorbed in the body, chlorinated pesticides are difficult to eliminate. Many are fat soluble and accumulate in the adipose tissue of mammalian species [24]. Long term pesticide exposure can lead to cancer, neuro-behavioural changes, liver abnormalities, kidney dysfunction and symptoms of psychological distress [25, 26, 27].

1.3 Pesticide detection in drinking water

1.3.1 Fate of pesticides in the environment

Ideally, a pesticide should reach the intended pest target, produce the desired effect and then break down into non-hazardous material. However, only 0.1 % of applied pesticides actually reach the target pest [28]. The remaining 99.9 % is dispersed throughout the environment, exposing handlers, residents and polluting air, soil and water systems.

The rate at which pesticides degrade in the environment is expressed in terms of half-life. This is the amount of time it takes until its concentration is half of its initial level. The half-life and migration of a pesticide depends on a variety of factors including chemical properties and mobility.

The chemical properties of pesticides and resistance to degradation are important factors contributing to pesticide pollution in the environment. The volatility of a pesticide determines how easily it evaporates and therefore how far it can travel through the air stream. The solubility of a pesticide can enhance its mobility. A water soluble pesticide can be carried by rainfall and leach into ground water. Water soluble pesticides can travel and accumulate in water streams, causing adverse effects in fish and aquatic organisms.

The migration is further affected by soil properties, rate and method of application, irrigation, rainfall and depth to ground water. The soil sorption coefficient, K_{oc}, is an index for pesticide mobility. If a pesticide is highly water soluble, is has a lower soil sorption coefficient. An example of pesticide half-life, water solubility and sorption coefficient data is shown in Table 1.5.

Biodegradation of pesticides may occur naturally in soil and water. Micororganisms such as bacteria, fungi and actinomycetes can interact both chemically and physically with pesticides, leading either to structural changes or complete degradation [29, 30, 31]. As pesticide contamination in lakes build up, the indigenous bacteria and algae build up resistances and start to dominate [32]. Cyanobacteria (blue-green algae) have become highly effective degraders of environmental pollutants [33, 34].

Table 1.5: Pesticide soil half-life, water solubility and soil sorption coefficient (K_{oc}) data [35].

Pesticide	Soil half-life (days)	Water solubility (mg/L)	Soil sorption coefficient (K_{oc})
Atrazine	60	33	100
Bromacil	60	700	32
Carbatyl	10	120	300
Chlorpyrifos	30	0.4	6070
Dicamba salt	14	400,000	2
Diuron	90	42	480
Simazine	60	62	130

1.3.2 Safeguards and standards

1.3.2.1 Drinking Water Standard

The quality of the water intended for human consumption within the European Union is subject to the Drinking Water Directive (DWD) Council Directive 98/83/EC. The purpose of the directive is to protect the health of the consumer and to ensure that the drinking water supply is fit for human consumption. The guidelines are modelled on the established WHO guidelines for drinking water quality. Member states publish reports every 3 years containing results for a total of 48 microbial and chemical parameters which must be monitored and tested regularly. This includes a parameter for both individual pesticide concentrations and a value for total pesticides. The total pesticide parameter is a sum of all individual pesticides detected and quantified. However, only pesticides which are likely to be present in the drinking water supply need to be monitored. The term "pesticide" used in the council directive applies to the following compounds;

- organic insecticides
- organic herbicides
- organic fungicides
- organic nematocides

- organic acaricides
- organic algicides
- organic rodenticides
- organic slimicides
- related products (inter alia, growth regulators) and their relevant metabolites, degradation and reaction products

The total amount of permissible individual pesticide in a water sample is 0.1 μg/L. In the case of aldrin, dieldrin, heptachlor and heptachlor epoxide the parametric value is 0.03 μg/L. This limit reflects the chronic toxicity reported for heptachlor and structurally related compounds [36]. A maximum value of 0.5 μg/L is acceptable for total pesticides detected.

1.3.2.2 Integrated Pest Management

Integrated Pest Management (IPM) is a concept used to control pests based on a series on common-sense practices [37, 38]. As part of the IPM approach, a series of evaluations, decisions and actions are required. Initially a threshold value is set for pest populations or environmental conditions which require action. Pests must be identified and monitored before any action is taken. This step is crucial because not all pests may be harmful or require action to be taken. Another approach within IPM is to plant crops which have been modified to resist pests. If, after consulting these steps, action still needs to be taken to control a pest, using less risky methods first such as pheromones to disrupt mating (insects), weeding or trapping are recommended. The use of pesticides should be a last resort.

An example of successful IPM implementation is shown in the evolution of the pear industry in California. This industry was one of the heaviest users of pesticides to control insects and mites in the 1960s. Over a 50 year period the industry has successfully scaled back their pesticide use from over 14 active ingredients to 3 - 5 mostly organic certified ingredients [39].

1.3.3 Persistence and detection in drinking water

Conventional drinking water treatment plants (DWTP) follow a simple working design [40, 41, 42, 43]. Surface water, usually from a lake or reservoir, enters the treatment plant and is initially filtered to remove large debris. The next process is coagulation/flocculation. Coagulant chemicals can be either metallic salts or polymers and are added to neutralise charged particles, causing them to collide and form flocs. The flocs then settle out of the water as sediment. The next step in the treatment process is filtration.This helps eliminate particulate matter including clays and silts, natural organic matter, precipitates from other treatment processes in the facility, iron and manganese, and microorganisms. Ion exchange processes are used to remove inorganic contaminants. Ion exchange can be used to treat hard water. It can also be used to remove arsenic, chromium, excess fluoride and nitrates. Organic contaminants, unwanted colouring, and taste and odour causing compounds are moved via adsorption to either granular or powder activated carbon. The last step of the treatment process before the water enters the distribution system is disinfection. Disinfection ensures that potentially dangerous microbes are killed. Chlorine, chloramines, or chlorine dioxide are most often used but other forms of disinfection such as ozone or ultraviolet radiation can be used.

Despite the existence of this complex treatment process, pesticides are often still detected in water intended for distribution. Any breach of the DWD guidelines must be reported. Figure 1.1 represents the monitoring results in the Republic of Ireland (ROI) as required by the DWD after an extensive monitoring program was launched in 2005. The graph shows the number of exceedances reported for individual and total pesticide concentrations. Since the monitoring program began, there has been a decrease in the number of exceedances reported each year. The latest report [44] for the period 2008 - 2009 showed that no individual herbicide concentrations were detected. However, there were still 2 exceedances for the total pesticide parameter.

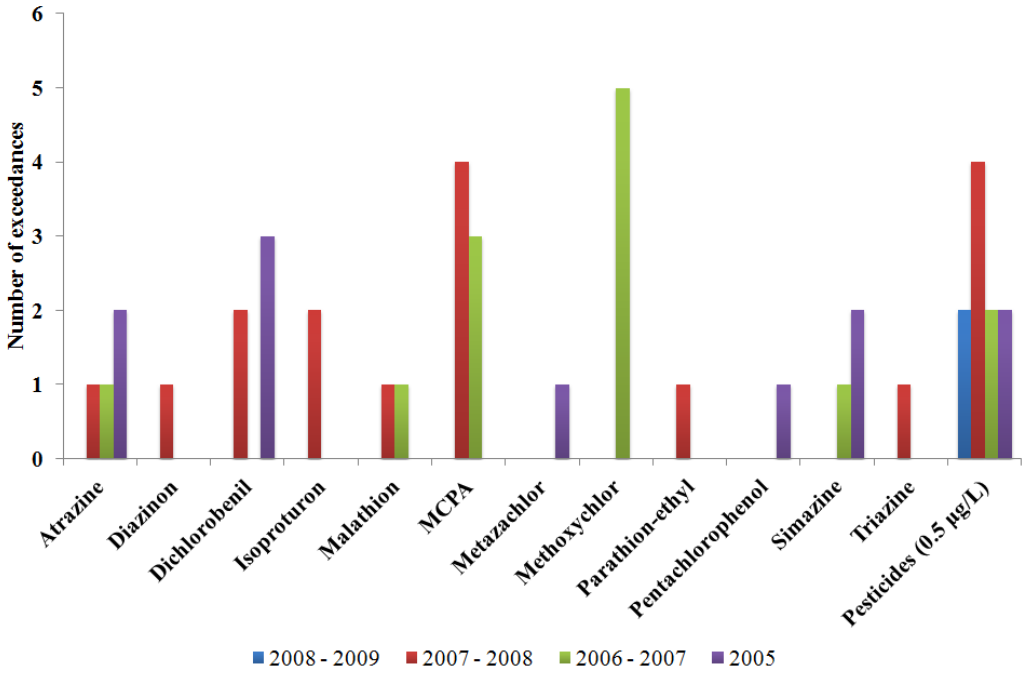
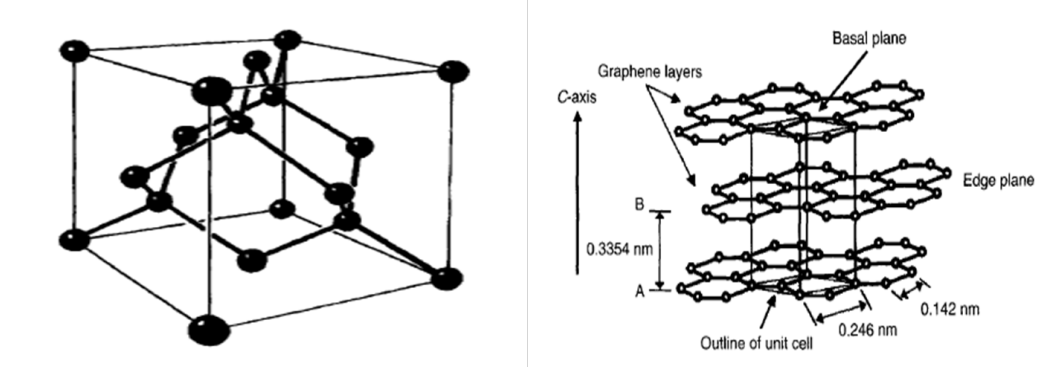


Figure 1.1: Chart showing the number of reported pesticide exceedances in drinking water supplies in ROI from 2005 - 2009 [45, 44, 46, 47, 48].

1.4 Activated Carbon

Charcoals (active or porous) have been used through out history for a number of different applications. Charcoal has been used for medicine, in gas mask filters, for fireworks, gunpowder and for purification. Today, activated carbon is used for purification and recovery in various industries. It is used for solvent recovery, gold and silver recovery, air purification and in the treatment of domestic and industrial waste and drinking water.

In nature, carbon can exist in several forms, distinguished by degrees of disorder. The two best known structures are in the form of graphite and diamond. The carbons in graphite have a planar hexagonal arrangement, described as graphene layers. The layers do not sit on top of each other but are offset (Figure 1.2 (b)) and held together by van der Waal forces. This type of graphite is referred to as AB graphite. The structure of diamond is more dense than graphite. The carbons are tightly packed with strong carbon-carbon bonds which contribute to the hardness associated with diamonds. The degree of disorder in the carbon structure increases between single crystal graphite, pyrolytic carbons and



(a) **(b)**

Figure 1.2: A model of the cubic unit cell of diamond (a) where the internal carbon atoms are bonded to three other carbon atoms with sp^3-symmetry and (b) the structure of hexagonal graphite showing trigonal planar bonding within the graphene layers [50].

polycrystalline graphites. The increase in disorder is where the graphene layers abandon the ABAB structure and eventually exhibit a smaller, defective structure. The defects create porosity within the activated carbon where a random bonding order between polycyclic groups of carbons and linear carbon atoms occur. The resulting porous structure is made up of a network of interconnected macro, meso and micropores (Figure 1.3) [49].

1.4.1 Preparation of activated carbon

Activated carbons can be prepared in laboratories from a large number of materials but the most commonly used materials for commercial carbons are peat, coal, wood, lignite and coconut shell. There are two main types of activation processes: physical and chemical activation.

1.4.1.1 Physical activation

The production of activated carbon by physical activation follows a three step process: oxidation of the material (e.g. coal), carbonisation into charcoal and then charcoal activation [51, 52, 53, 54]. The oxidation process changes the chemical composition of the material. Carbonisation of the oxidised material eliminates volatiles and produces a fixed carbon mass with a primary pore structure. The porous structure produced is either too small or

constricted for it to be useful as an adsorbent. Activation increases pore volume and widens micropores produced during carbonisation and creates new porosity. Activation by carbon dioxide or steam extracts carbon atoms from the pore walls and thereby enlarges them. The process is an endothermic reaction described as follows:

$$C + CO_2 \rightleftharpoons 2CO \qquad \text{(Reaction 1.1)}$$

$$C + H_2O \rightleftharpoons CO + H_2 \qquad \text{(Reaction 1.2)}$$

Activation by molecular oxygen is an exothermic reaction which unless controlled, yields no enhancement of the porosity because the molecular oxygen consumes the carbon. Controlled reactions with molecular oxygen at 600 °C and $>$ 900 °C favour the formation of carbon dioxide and carbon monoxide, respectively.

$$2C_f + O_2 \rightleftharpoons 2CO \qquad \text{(Reaction 1.3)}$$

$$C_f + O_2 \rightleftharpoons CO_2 \qquad \text{(Reaction 1.4)}$$

C_f describes a carbon atom which is free from bonding with surface complexes and is therefore available for reaction with an oxygen molecule. Generally, physical activation is used in the production of granular activated carbon (GAC).

1.4.1.2 Chemical activation

Chemically activated carbons are produced by mixing a chemical with a ligneous materially (usually wood) and then carbonizing the mixture. Activation temperatures are lower than those needed for physical activation and are generally between 400 °C and 500 °C. The chemicals used for this type of activation are usually either phosphoric acid or a zinc chloride solution, which can be recovered and recycled after activation. In the case of chemical

activation, the porosity is created when the chemicals cause the wood structure to swell and open up the cellulose structure. The output of chemical activation is usually in the form of powdered activated carbon (PAC).

1.4.2 Liquid phase application

Since 1930, PAC has been used to purify ground water, making it suitable to drink. The implementation of AC for liquid phase adsorption clarified the water, and removed bad tastes and odours. Treatment with PAC, however is based on a dosing system where PAC is added when needed and then removed by filtration. It is discarded after use and is not reused. GAC is used in fixed bed applications and can be regenerated by using either steam or chemicals once the activated carbon has lost some of its adsorption capability.

Adsorption of organic compounds by activated carbon is controlled by two processes; physical interactions and chemical interactions [55, 56, 57, 58, 59, 60, 61]. Physical interactions are based around the structure of the activated carbon (Figure 1.3) and include size exclusion and microporosity. The majority of the surface area available for adsorption is located in the micropores. Size exclusion can inhibit access to the finer pores for macromolecules, while still allowing access to to adsorption sites for smaller molecules. When the molecule dimensions approach the width of the pores, multiple points of contact become possible for adsorption and surface forces overlap. Chemical interactions are influenced by the molecular structure of the adsorbate, surface chemistry of the carbon, and solution chemistry. Chemical interactions can relate to hydrophobic interactions between adsorbate and solvent or interactions between adsorbate and the carbon surface. The adsorbate can interact with the carbon surface in a number of ways; non-specific dispersion forces, basal plane electrons, unpaired electrons located on the edges of terminated basal planes and surface functional groups. Furthermore, electrostatic interactions can be influenced by pH and ionic strength.

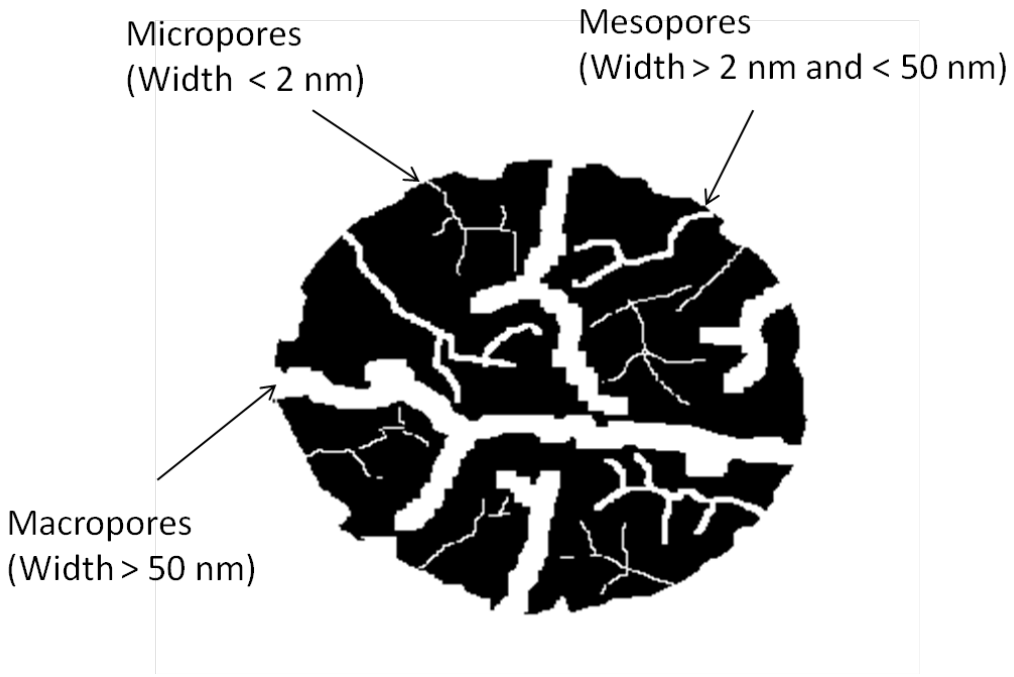


Figure 1.3: Activated carbon schematic demonstrating the size distribution of micro, meso and macropores

1.4.3 Adsorption isotherms for single component systems

The specific capacity of an activated carbon to adsorb organic compounds is related to: molecular surface attraction, the total surface area available per unit weight of carbon, and the concentration of contaminants. Adsorption processes are usually described by graphs known as adsorption isotherms. The isotherm represents an empirical relationship between the amount of contaminant adsorbed per unit weight of carbon and its equilibrium water concentration.

The Langmuir isotherm

In 1918, Langmuir proposed the first isotherm model which assumed monolayer coverage of the adsorbent. The model contained several assumptions:

- All molecules are adsorbed on defined sites on the adsorbent surface

- Each site can only be occupied by one molecule (monolayer coverage)
- The adsorption energy of all sites is equal
- There is no interaction between molecules occupying neighbouring sites

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1.1}$$

Where, q_m (mmol/g) is the maximum amount of herbicide per unit weight of adsorbent covering the surface in a monolayer fashion at high C_e (mmol/L) and K_L (L/mmol) is the Langmuir constant relating to the affinity of the binding sites. The prediction of favourable or unfavourable adsorption can be obtained by calculating the separation factor (R_L) defined as:

$$R_L = \frac{1}{1 + K_L C_e} \tag{1.2}$$

Here R_L is the dimensionless separation factor, K_L is the Langmuir constant calculated from (1.1). Adsorption performance can be classified as follows;

$R_L > 1$ Unfavourable

$R_L = 1$ Linear

$R_L < 1$ Favourable

$R_L = 0$ Irreversible

The Freundlich isotherm

The empirical Freundlich equation (1.3) is used to describe the adsorption of heterogeneous systems:

$$q = K_F C_e^{\frac{1}{n}} \tag{1.3}$$

Where the Freundlich parameters K_F describes the adsorption capacity as a parameter of heterogeneity and n indicates the adsorption intensity. Values for n between 2-10 are favourable whereas values above 10 indicate irreversible adsorption processes.

1.5 Liquid-core microcapsules

The original concept of encapsulation is to protect the contents of the capsule from the outside environment. Examples of encapsulation such as eggs, seeds, cells and spores can be found in nature. Encapsulation techniques are extensively used in agriculture, food, cosmetic and textile industries. Microencapsulation is a process whereby a substance is packed within a second material or coated with a continuous film of polymeric material. The substance encapsulated can be droplets, particles of liquid or solid material and is usually referred to as the inner core, internal phase, encapsulate or fill. The material used to encapsulate the inner core is often referred to as the outer wall, shell, external phase or membrane.

A novel concept for the removal of environmental pollutants from aqueous environments has previously been reported [62, 63, 64, 65, 66, 67]. The process involves the envelopment of pre-selected organic solvents within a porous hydrogel membrane to form liquid-core microcapsules. These can be used to extract and retain persistent organic pollutants. There are many ways to produce microcapsules by either chemical, physico-chemical or physico-mechanical processes. The shape and structure of a microcapsule is dependant on the encapsulation process. The structures which may be produced are depicted in Figure 1.4.

1.5.1 Inner core materials

Core materials can be either solid, liquid or gas. Core examples include; 1) pigments, 2) dyes, 3) monomers, 4) catalysts, 5) flame retardants, 6) plasticizers, 7) nanoparticles.

1.5.2 Shell materials

The shell must be inert with respect to the inner core. The shell can be permeable, semi-permeable or impermeable. Permeable shells allow for the release of the inner core. Semi-permeable cores are impermeable to the core material but are permeable to low molecular weight liquids. Impermeable shells must be mechanically ruptured, melted, dried out or dissolved to release the inner core material. The shells are typically composed of;

- Non-biodegradable synthetic polymers (e.g. epoxy polymers, acrolein, glycidyl methacrylate)
- Biodegradable synthetic polymers (e.g. polyanhydrides, lactides, glycolides)
- Natural materials (e.g. proteins, gelatin, carrageenan)
- Chemically modified carbohydrates (e.g. poly (acryl) dextran, poly (acryl) starch, DEAE cellulose)

1.5.3 Production of microcapsules

The following section briefly describes some of the processes employed in the manufacture of liquid core microcapsules. Microencapsulation methods and expected microcapsule size produced from these methods are listed in Table 1.6.

Co-extrusion

Capsules are produced from a dual fluid stream of liquid core and shell material, pumped through a concentric nozzle. Droplets are formed under the influence of vibration at a

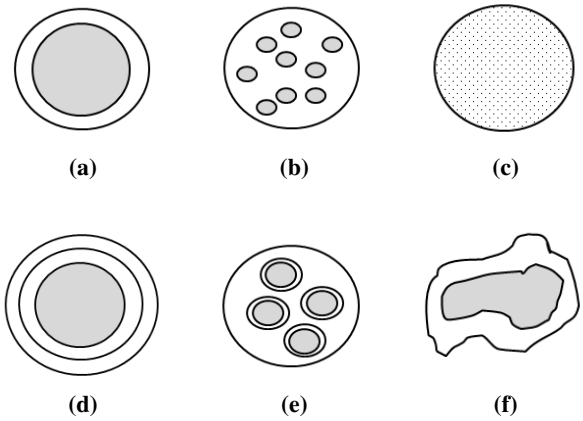


Figure 1.4: Various microcapsule structures: (a) mononuclear type, (b) polynuclear type, (c) matrix type, (d) multi-wall type, (e) micro-encapsulated, and (f) irregular shaped [68, 69].

Table 1.6: Microencapsulation methods and expected microcapsule size [70].

Microencapsulation process	Casule size (μm)	Type of process
Extrusion	250 - 2500	Physico - mechanical
Spray drying	5 - 5000	Physico - mechanical
Fluid bed coating	20 - 1500	Physico - mechanical
Rotating disk	5 - 1500	Physico - mechanical
Coacervation	2 - 1200	Physico - chemical
Solvent evaporation	0.5 - 1000	Chemical
Phase separation	0.5 - 1000	Chemical
In-situ polymerisation	0.5 - 1100	Chemical
Interfacial polymerisation	0.5 - 1000	Chemical
Miniemulsion	0.1 - 0.5	Chemical
Sol-gel encapsulation	2 - 20	Physico - chemical
Layer-by-layer assembly	0.02 - 20	Physico - chemical

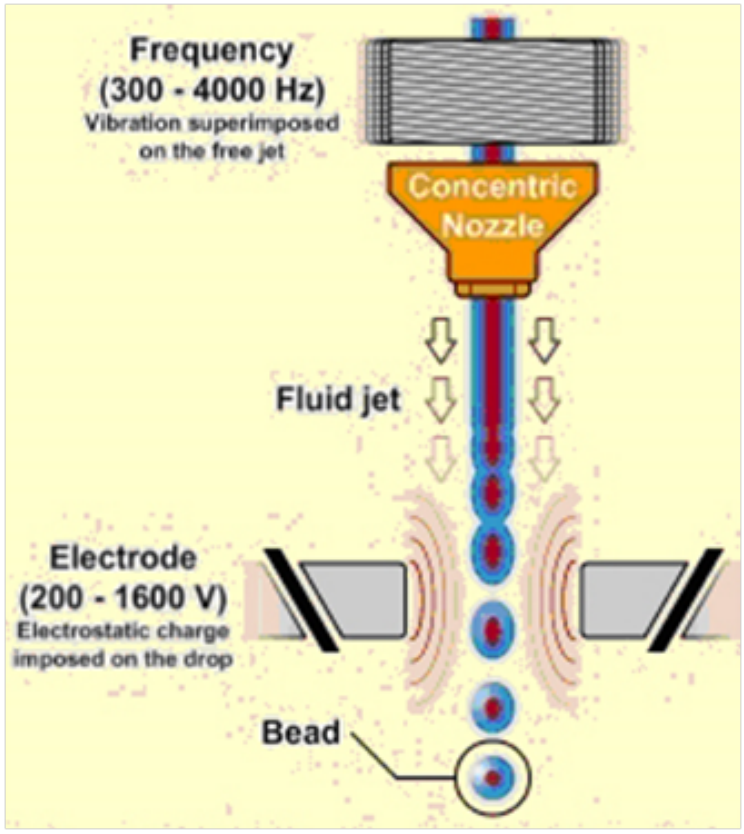


Figure 1.5: Schematic showing the co-extrusion process [71]

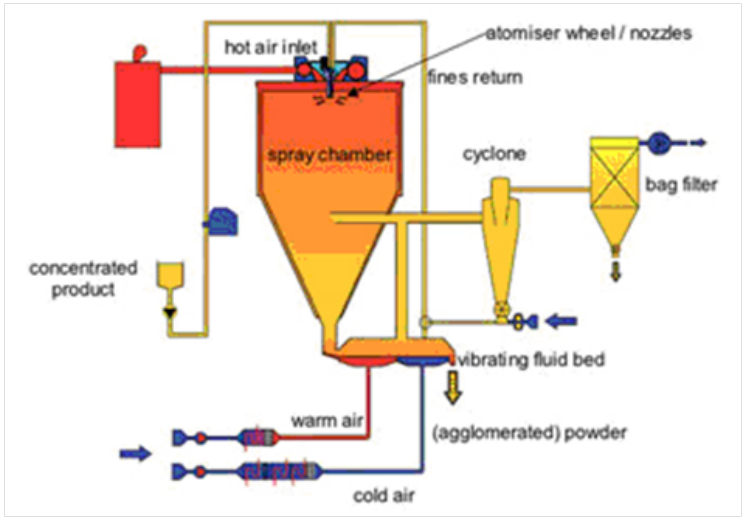


Figure 1.6: Schematic showing the spray drying process [71]

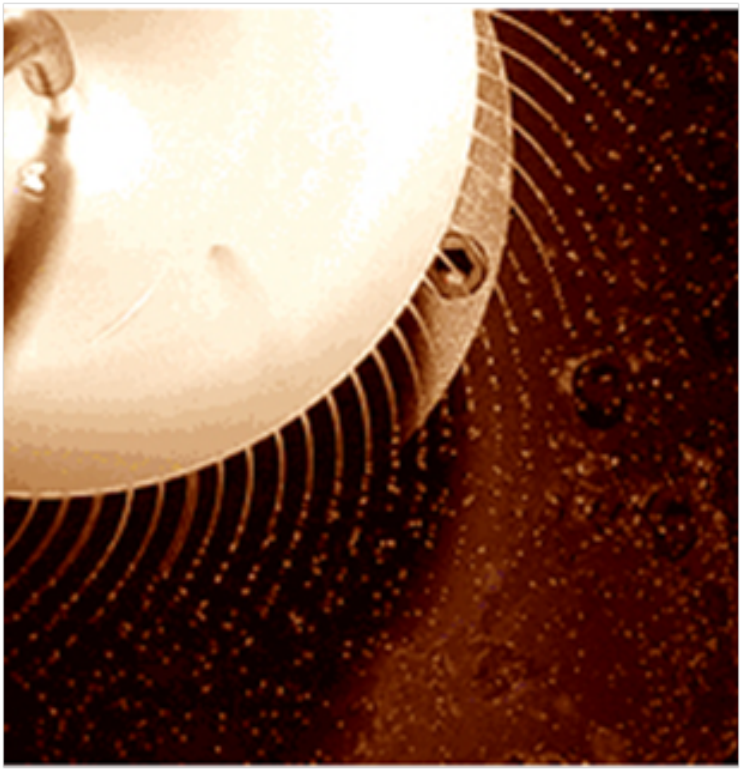


Figure 1.7: Image depicting the rotating disc process [71]

set frequency (Figure 1.5). The shell material is then hardened by chemical cross linking, cooling or solvent extraction.

Spray drying

Polynuclear or matrix type capsules are produced when core particles are dispersed in a polymer solution and sprayed into a hot chamber, allowing the shell material to solidify onto the core particles as the solvent evaporates. A schematic of the spray drying process is shown in Figure 1.6.

Fluidised bed technology

Solid or porous particles are encapsulated by spraying on a liquid coating which then quickly evaporates, leaving an outer layer on the particle. Spraying can be either top spray, bottom spray or tangential spray.

Rotating disc

Suspensions of core particles in liquid shell material are poured into a rotating disc. The

spinning action of the disc causes the core particles to become coated with the shell material. The coated particles and the excess shell material are then cast from the edge of the disc by centrifugal force (Figure 1.7). Shell material is solidified by external means (e.g. cooling).

Miniemulsion

Nanocapsules of high stability in a continuous phase are created using high sear ultrasound or high pressure homogenizer techniques. The capsules are produced in two stages. First droplets are formed by shearing a system containing the dispersed phase, continuous phase, a surfactant and osmotic pressure agent. The second step is polymerization achieved by either; polyaddition, polycondensation, anionic polymerization, metal-catalyzed polymerization reactions or enzymatic polymerization.

1.6 Project proposal

The aim of the following work is to remove three chlorophenoxy herbicides from aqueous solutions. The three herbicides of interest are MCPA, 2,4-D and dichlorprop. These herbicides present a reoccurring problem for the drinking water industry when levels of these are found in water samples intended for distribution. It is envisaged that the removal of herbicides from aqueous solution will take place in two ways; 1) adsorption to activated carbon and 2) perstraction (term is derived from permeation and extraction [72]) by a novel technique incorporating liquid core microcapsules (LCMs).

The activated carbon used in this project will be to the same specifications currently used in DWTP. The project aims to compare the adsorption efficiency of activated carbon to that of mononuclear (Figure 1.4 (a)) liquid core microcapsules, which have previously shown high removal efficiencies for organics, for example the pesticide atrazine [66], from solution. In contrast to conventional liquid-liquid extraction approaches the technology is clean, leaves no solvent residues in the water, does not form stable emulsions and microcapsules may be readily separated from the water through filtration/flotation. LCMs have high mass transfer area for rapid, efficient extraction and selectivity may be adjusted through choice of liquid-

core material and hydrogel membrane properties.

Although herbicide concentrations in real water samples are generally below the 0.1 μg/L drinking water guidelines, this study will work with higher concentrations which would not typically be found in drinking water samples. This approach will ensure that the concentration of herbicide remaining in the water samples after adsorption/perstraction will be sufficient for a quantitative analysis. If lower concentrations were used, the residual herbicide concentrations could be below the instrumental limit of detection and therefore yield no quantitative data.

In addition to this comparison, we will attempt to investigate why activated carbon filters used in DWTP are not always effective at removing these particular pollutants from drinking water . The drinking water industry is keen to investigate potential causes for these failures. The chosen approach will focus on the potential fouling of activated carbon by natural organic matter (NOM), in particular, humic acid (HA).

1.7 Project strategy

The project strategy to meet the aims discussed in the previous section is as follows:

Analytical method development:

A suitable method will be developed and validated to determine quantitatively the residual concentration of each herbicide in aqueous solution.

Activated carbon comparison:

Batch adsorption experiments will compare the adsorption capacity of two GACs and one PAC used in DWTP. Additionally a laboratory grade AC was also tested to compare efficiency to DWTP AC.

pH study:

pH studies in buffered solutions will be implemented to see if the AC adsorption capacity is affected.

Adsorption isotherm analysis:

Experimental data will be fitted to the commonly used Langmuir and Freundlich isotherm models.

Humic acid adsorption to AC:

Humic acid adsorption to GAC will be investigated.

Herbicide adsorption to AC fouled by humic acid:

The effect of humic acid fouling on herbicide adsorption to GAC will be investigated. The AC used to adsorb humic acid will be recovered and reused in order to evaluate and compare the adsorption capacity to virgin AC used previously.

Liquid core microcapsule production:

The production of liquid core microcapsules previously used by Wyss et al [66] to remove atrazine will be reproduced used to extract MCPA, 2,4-D and dichlorprop.

Liquid core microcapsule oil core selection:

A new oil core for LCMs for the extraction of the target herbicides will be selected by results obtained from liquid-liquid extraction experiments.

New LCM production:

Upon selection of a new oil core, the encapsulation of the new core will be attempted.

Comparison between AC and LCM:

Data generated from AC and LCM experiments will be compared. This could determine the feasibility of commercial application of LCMs.

Chapter 2

The development and validation of a rapid high performance liquid chromatography (HPLC) detection method for MCPA, 2,4-D and dichlorprop chlorophenoxy herbicides

2.1 Introduction

The current project focuses on the removal of chlorophenoxy herbicides from water. The herbicide concentration in the water sample after either activated carbon adsorption or liquid-core microcapsular perstraction must therefore be quantifiable. The U.S. Environmental Protection Agency (EPA) recommend using a capillary gas chromatographic (GC) method [73] to quantify chlorinated herbicide residues in aqueous, soil and waste matrices. This includes the detection of the herbicides MCPA (4-chloro-2-methylphenoxy acetic acid), 2,4-D (2,4-dichlorophenoxy acetic acid) and dichlorprop (2-(2,4-dichlorophenoxy) propionic acid) featured in this project.

However, MCPA, 2,4-D and dichlorprop are non-volatile polar herbicides and require further derivatization to form thermally stable compounds for gaseous phase analysis. This additional derivatization process, equipment access and the need for an auto-sampler means the use of GC analyses was not feasible for the planned experiments. However, high performance liquid chromatography (HPLC) analyses was available. HPLC analyses facilitates the need for residual concentration analysis which do not require pretreatment or derivatization.

2.2 Materials and methods

2.2.1 Reagents and preparation of standards

Technical grade ($>$ 97 %) herbicides MCPA (4-chloro-2-methylphenoxy acetic acid) and 2,4-D (2,4-dichlorophenoxy acetic acid) were supplied by Fluka (Dublin, Ireland). Technical grade ($>$ 98 %) herbicide dichlorprop (2-(2,4-dichlorophenoxy) propionic acid) was purchased from Alfa Aesar (Lancashire, United Kingdom). HPLC grade water and methanol were purchased from Fisher Scientific (Dublin, Ireland). Formic acid (mass spectrometry grade) and ammonium acetate were purchased from Sigma Aldrich (Dublin, Ireland). Ultra–pure water was obtained from a Millipore Milli-Q water purification unit.

Herbicide stock solutions (10 mmol/L) were prepared by dissolving the compounds in methanol. Stock solutions were stored in the fridge at 4 °C in amber glass bottles until required. Standards were prepared by serial dilution from the stock and diluted with ultra-pure water before being transferred to amber glass HPLC vials.

2.2.2 High performance liquid chromatography

RP-HPLC was performed on a Agilent 1100 (Agilent Technologies, Palo Alto, Ca, USA) series equipped with a vacuum de-gasser, quaternary pump, ALS auto-sampler and variable wavelength detector. Agilent Chemstation version B.02.01-SRI (Agilent Technologies, Palo Alto, Ca, USA) was employed for data analysis. Herbicide standards were prepared as described in Section 2.2.1 and transferred to 2 mL amber HPLC vials complete with PTFE lids (Fisher Scientific, Dublin, Ireland). The mobile phases were filtered through a PALL nylon filter (0.2 μm) and degassed by sonication for 60 minutes. Standards were injected on to a Luna C18 (Phenomenex, Cheshire, United Kingdom) analytical column with dimensions measuring 4.6 x 150 mm, a particle size of 5 μm and equipped with an associated SecurityGuard guard column (Phenomenex, Cheshire, United Kingdom).

2.2.2.1 Gradient multicomponent analysis

Two method conditions, labelled X and Y, were used for multicomponent analysis of MCPA and 2,4-D. Method X mobile phases consisted of an aqueous mobile phase (AX) containing 90 % water containing 0.1 % ammonium acetate buffer, and 10 % methanol. The organic mobile phase (BX) was made up of 90 % methanol, and 10 % water containing 0.1 % ammonium acetate buffer. The mobile phase used in method Y had the same percentages of water and methanol for both aqueous and organic mobile phases but the 0.1 % ammonium acetate was replaced with 1 % formic acid. The gradient times and conditions for both methods are listed in Table 2.1 and Table 2.2.

Table 2.1: Gradient HPLC conditions X used to develop a method for multicomponent analysis of 2,4-D and MCPA

Gradient	Time (min)	AX %	BX %
	0	90	10
	1	90	10
	9	0	100
	16	0	100
	25	90	10
	30	90	10
Buffer	Ammonium acetate		
pH	5.5		
Flow rate	0.8 mL/min		
Injection volume	20 μL		
Detection λ	270 nm		

Table 2.2: Gradient HPLC conditions Y used to develop a method for multicomponent analysis of 2,4-D and MCPA

Gradient	Time (min)	AY %	BY %
	0	90	10
	1	90	10
	9	0	100
	16	0	100
	25	90	10
	30	90	10
Buffer	Formic acid (1 %)		
pH	2		
Flow rate	1 mL/min		
Injection volume	50 μL		
Detection λ	270 nm		

2.2.2.2 Isocratic single component analysis

The mobile phase consisted of 80 % (v/v) methanol and 20 % (v/v) water containing 1 % (v/v) formic acid. The flow rate was controlled at 1 mL/min and all herbicides were detected separately at wavelengths of 279 nm, 284 nm and 285 nm for MCPA, 2,4-D and dichlorprop respectively. The herbicide detection wavelengths were selected based on the absorbance spectra obtained for 0.1 mmol/L herbicide samples. UV-Visible spectroscopic measurements were performed between 200 and 470 nm on a Perkin Elmer (Perkin Elmer, Waltham, MA, USA) Lambda 900 double beam spectrophotometer using a 1 cm quartz

cuvette.

2.2.3 Validation procedure and criteria

The chromatographic method development criteria was adapted from guidelines issued by the International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH) [74], the U.S. Pharmacopoeia (USP) [75], and the U.S. Food and Drug Administration (FDA) [76].

2.2.3.1 Precision

The method precision was calculated to demonstrate the ability of the method to produce consistent results. The precision was determined by injecting 0.6 mmol/L herbicide standard (n=6) replicates. The precision was expressed as the relative standard deviation (RSD). The criteria for peak area and retention time variation is $<1\%$ RSD.

2.2.3.2 Accuracy

The method accuracy determined the closeness of agreement between the measured standards and their theoretical concentration. Accuracy considers errors associated with sampling, sample preparation and sample analysis. Accuracy should be in agreement with 100 $\% \pm 2\ \%$ of the theoretical concentration.

2.2.3.3 Limit of Detection (LOD)

The limit of detection (LOD) is defined as the lowest concentration of an analyte that can be detected but not necessarily quantified under the experimental conditions of the method. LOD can be determined from the standard deviation of the responses and the slope of the calibration curves. Although there is no specific criteria for LOD, the detection limit should be sufficiently low to allow for analysis above and below the required range.

2.2.3.4 Limit of quantitation (LOQ)

The limit of quantitation (LOQ) is defined as the lowest concentration of analyte in a sample that can be quantified while still meeting all other method validation requirements (accuracy, precision, linearity etc.).

2.2.3.5 Linearity and range

The linear range is described as the response vs. concentration and can have either a linear or non-linear relationship. The linear relationship is dependent on the compound analysed and the detector used. In the case of a UV-Visible detector, the linear relationship is controlled by the Beer Lambert Law. Linearity should be visible with a regression coefficient (R^2) $>$ 0.999. The linear range investigated for this validation procedure was 0.01 - 1 mmol/L. Each sample was injected six times to ensure precision was maintained and an average of these injections was plotted to obtain the regression coefficient.

2.2.3.6 Capacity factor

The capacity factor (k') is a measure of where the peak of interest is located with respect to other peaks or the void volume. The peaks should be well resolved and generally the value of k' should be $>$ 2. Peaks which are not well resolved are difficult to quantify.

2.2.3.7 Tailing factor

The tailing factor (T) is a measure of peak symmetry whereby a perfectly symmetrical peak has a T value equal to 1. Precision and quantitation becomes less reliable as peak asymmetry increases. This is due to an increased difficulty for the integrator in determining peak start and end points and calculating the peak area. It is recommended that T should be $<$ 2.

2.2.3.8 Theoretical plates

Column efficiency can be measured by a mathematical model describing a number of theoretical plates. Theoretical plates were first introduced by Martin and Synge [77] who described a column divided into a number of equal sections or plates where solutes could achieve equilibrium between two phases (mobile and stationary). When the mobile phase moves from one phase to the next, a new equilibrium is established.

2.3 Results and discussion

2.3.1 UV-Visible profiles and wavelength selection for HPLC

The UV-Visible profiles for MCPA, 2,4-D and dichlorprop reflect their similar structures. The structures of MCPA and 2,4-D differ by a chlorine substituent ortho to the acid group. Dichlorprop also contains a chlorine at this position and a propionic acid group rather than an acetic acid group. Figure 2.1 shows the UV-Visible absorption profile for MCPA at 0.1 mmol/L. The spectrum shows two major absorbances in the UV region of the spectrum at 228 nm and 279 nm. The molar absorptivity coefficient (ε) calculated from standard curves was found to be 1476 $M^{-1}cm^{-1}$ at 279 nm. The UV-Visible profile for 2,4-D at 0.1 mmol/L (Figure 2.2) shows two major absorbances at 229 nm and 284 nm. The molar absorptivity coefficient (ε) calculated from standard curves was found to be 1712 $M^{-1}cm^{-1}$ at 284 nm. Figure 2.3 shows the UV-Visible absorption profile for dichlorprop with two major absorbances at 229 nm and 285 nm. The molar absorptivity coefficient (ε) calculated from standard curves was found to be 1621 $M^{-1}cm^{-1}$ at 285 nm.

2.3.2 Method development

2.3.2.1 Gradient method development for multicomponent analysis

A gradient method was employed to try and separate MCPA and 2,4-D retention peaks in a single sample injection. Initial injections with method X for individual 2,4-D and MCPA

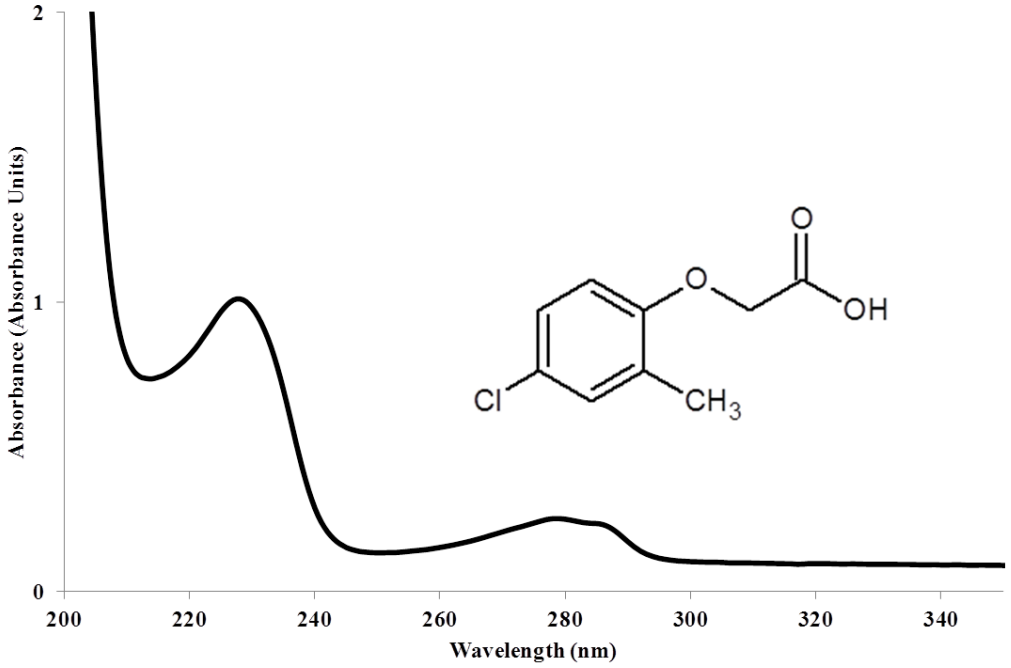


Figure 2.1: UV-Visible spectrum for MCPA at 0.1 mmol/L.

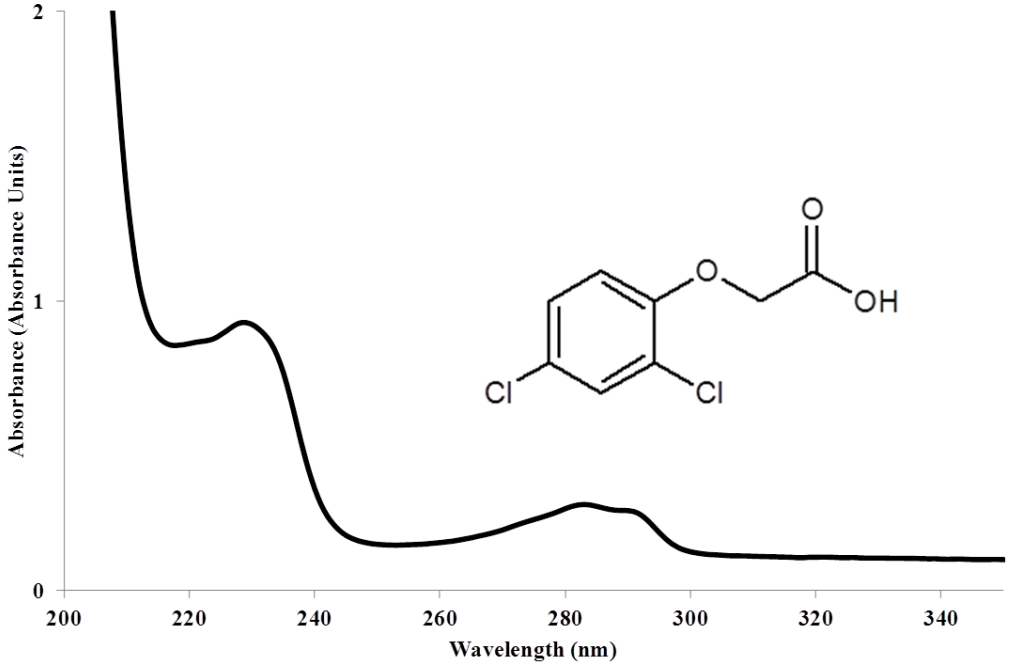


Figure 2.2: UV-Visible spectrum for 2,4-D at 0.1 mmol/L.

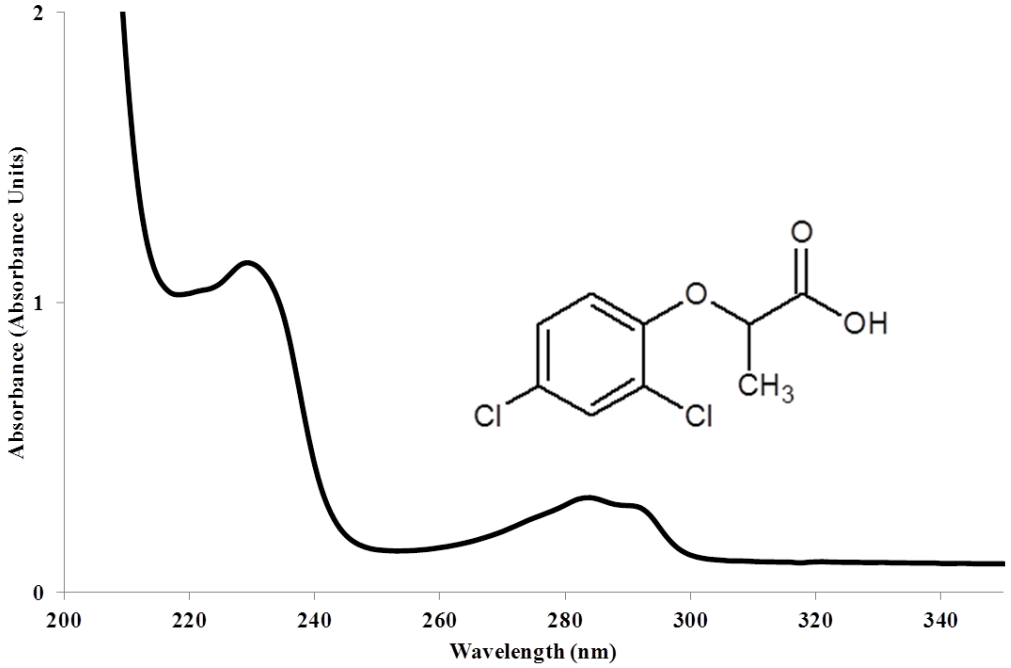


Figure 2.3: UV-Visible spectrum for dichlorprop at 0.1 mmol/L.

peaks are shown in Figures 2.4 and 2.5. 2,4-D and MCPA had a retention time of 10.047 and 11.011 minutes respectively. When a sample containing the same concentration of both herbicides was injected, the resulting peak observed, as shown in Figure 2.6, had a retention time of 11.077 and appeared as one peak. However, the peak area of this peak was the sum of both peak areas recorded for individual 2,4-D and MCPA samples. To facilitate separation of the two acidic herbicides, the mobile phase pH was lowered from pH 5.5 to 2 by substituting ammonium acetate with formic acid. When method Y was applied, the resulting multicomponent peak, as shown in Figure 2.7, was partially separated. Although partial separation was achieved, further and complete separation of two compounds differing by a chlorine group would be difficult to achieve and validate.

2.3.2.2 Isocratic method development for single component analysis

An isocratic method was developed as described in Section 2.2.2. An overlay of peak responses for MCPA, 2,4-D and dichlorprop can be seen in Figure 2.8.

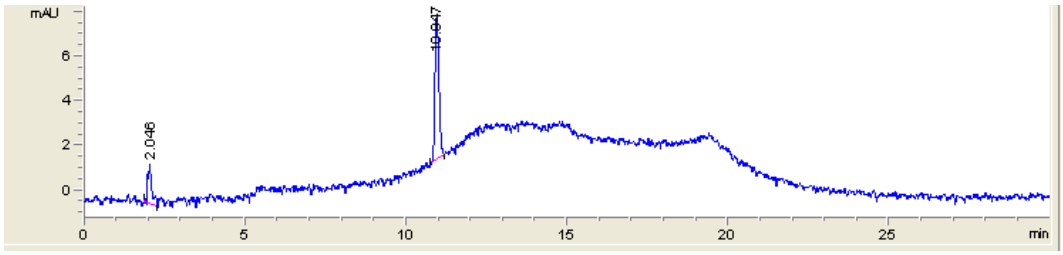


Figure 2.4: HPLC chromatograph showing a 2,4-D peak using gradient X conditions.

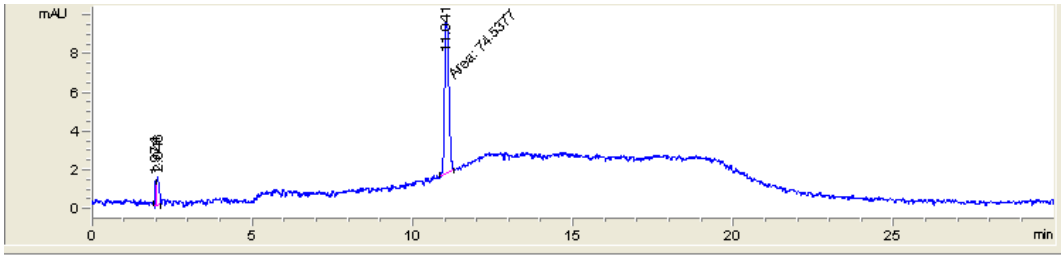


Figure 2.5: HPLC chromatograph showing a MCPA peak using gradient X conditions.

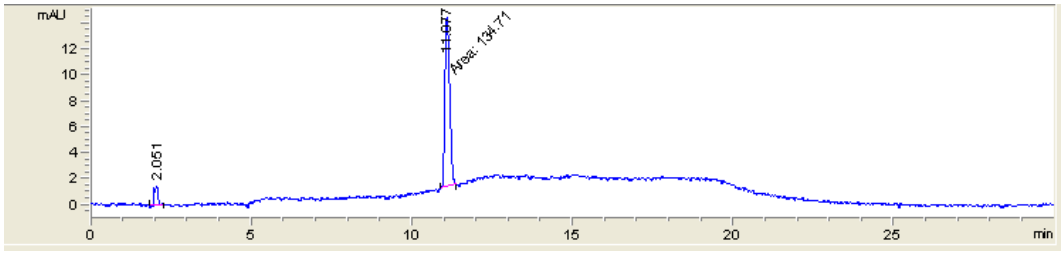


Figure 2.6: HPLC chromatograph showing a peak formed from a multicomponent sample containing 2,4-D and MCPA using gradient X conditions.

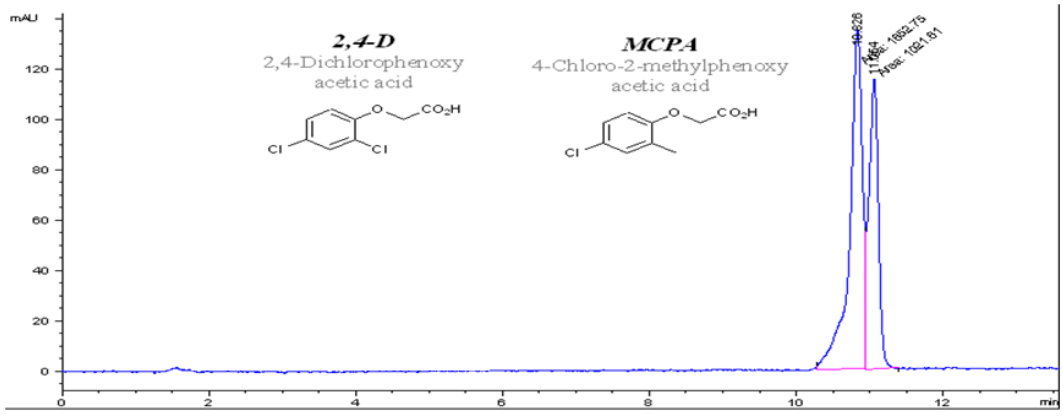


Figure 2.7: HPLC chromatograph showing a peak formed from a multicomponent sample containing 2,4-D and MCPA using gradient Y conditions.

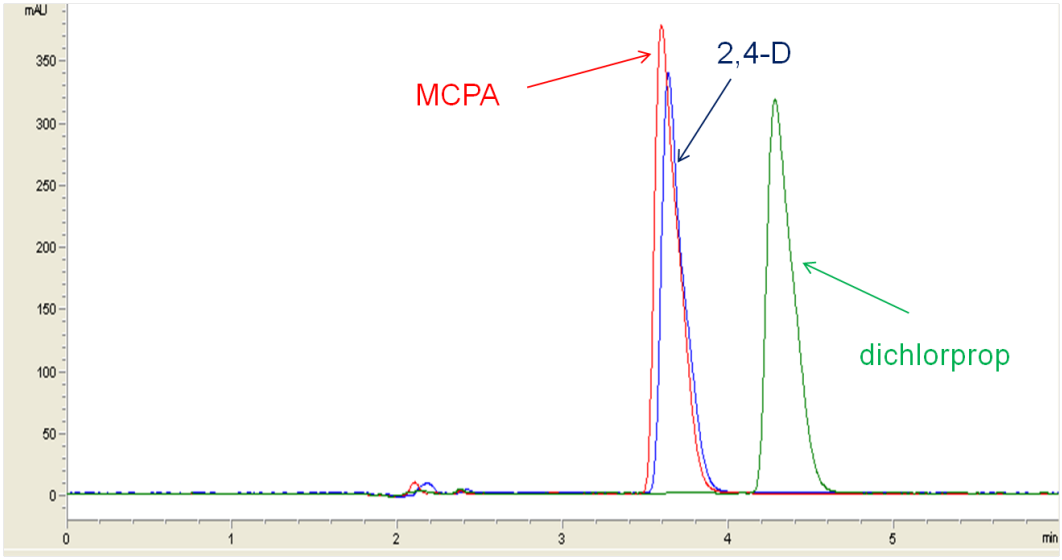


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Figure 2.8: HPLC chromatograph overlay of peak responses from the developed isocratic method for MCPA (blue), 2,4-D (red) and dichlorprop (green) at 0.6 mmol/L concentration.

2.3.3 Injection volume response

The injection volume response was determined by injecting varying volumes of MCPA standard on to the HPLC column. The volumes injected varied from 20 to 50 μL. The peak overlap displayed in Figure 2.9 shows the increase in peak area response which was dependant on the injection volume. The increased injection volume did not adversely effect the peak shape or retention time. Therefore, based on the increased UV response and good peak shape, 50 μL injection volume was used.

2.3.4 Validation

Method validation is a process of proving that an analytical method is suitable for the purpose. The method validation was performed as described in Section 2.2.3.

The precision parameter demonstrates the ability of an analytical method to produce consistent results. The agreement between n=6 injections are listed in Table 2.3 - 2.5. The precision results for peak area and retention time were below the acceptance criteria of ≤ 1 % RSD.

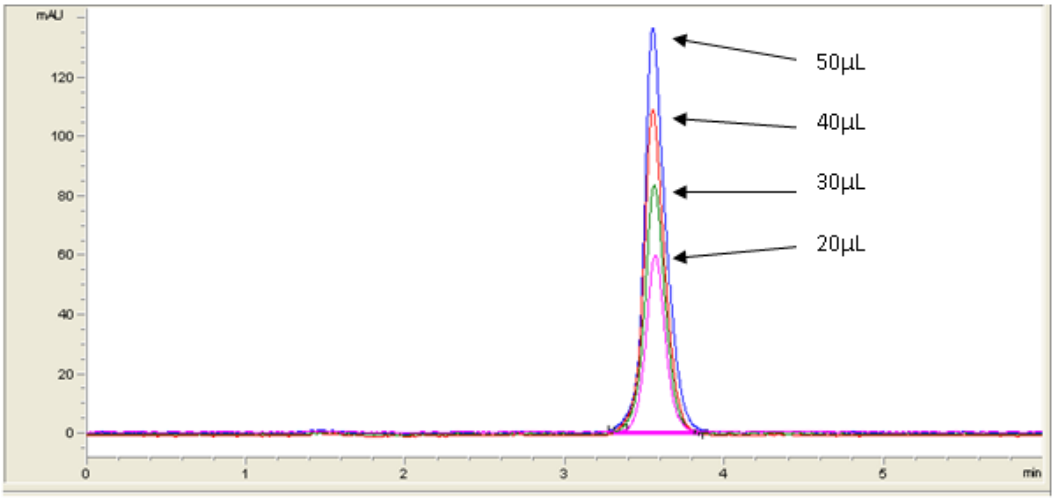


Figure 2.9: MCPA chromatograph detailing the peak area response obtained by varying the injection volume from 20 to 50 μL.

Table 2.3: Precision samples for MCPA chromatograph peaks at 0.6 mmol/L concentration.

Injection number	Peak area (AU)	Retention time (min)
1	3109.7	3.630
2	3097.3	3.620
3	3105.7	3.621
4	3103.1	3.624
5	3094.5	3.620
6	3094.6	3.617
Average	3100.8	3.622
Standard deviation	6.31	0.005
%RSD	0.20	0.12

Table 2.4: Precision samples for 2,4-D chromatograph peaks at 0.6 mmol/L concentration.

Injection number	Peak area (AU)	Retention time (min)
1	3726.4	3.584
2	3727.0	3.597
3	3719.3	3.594
4	3725.7	3.593
5	3726.5	3.594
6	3723.0	3.590
Average	3724.7	3.592
Standard deviation	2.98	0.005
%RSD	0.08	0.13

Table 2.5: Precision samples for dichlorprop chromatograph peaks at 0.6 mmol/L concentration.

Injection number	Peak area (AU)	Retention time (min)
1	3453.4	4.260
2	3448.6	4.256
3	3453.3	4.262
4	3449.4	4.255
5	3448.2	4.257
6	3453.5	4.256
Average	3451.1	4.258
Standard deviation	2.59	0.003
%RSD	0.08	0.06

The accuracy results for MCPA, 2,4-D and dichlorprop were 101, 99 and 100 % , respectively. These results were within the 100 % $\pm$ 2 % acceptance limit.

Linearity / range was evaluated over a range from 0.01 mmol/L to 1 mmol/L. The samples were injected six times to ensure precise results were obtained. From this data, a graph of the average peak area counts vs. the herbicide concentration was plotted. A regression line was applied to the graph and a linear relationship was observed for the full range analysed. The relevant statistics for MCPA, 2,4-D and dichlorprop are listed in Table 2.6. The correlation coefficient for each herbicide range was within the accepted criteria of > 0.999.

Table 2.6: Linear regression statistics for MCPA, 2,4-D and dichlorprop average (n=6) samples at 0.01 mmol/L - 1 mmol/L.

Herbicide	Slope	y-intercept	Correlation coefficient
MCPA	5216.7	-19.324	0.9996
2,4-D	6214.6	-2.157	0.9999
dichlorprop	5807.0	-17.615	0.9997

The limit of detection for MCPA, 2,4-D and dichlorprop was 0.0022 mmol/L, 0.0011 mmol/L and 0.0040 mmol/L respectively. The limit of quantitation for MCPA, 2,4-D and dichlorprop was 0.0067 mmol/L, 0.0035 mmol/L and 0.0121 mmol/L respectively.

The chromatographs obtained for each herbicide at 0.6 mmol/L were analysed for peak tailing, theoretical plate number and capacity factor. The values obtained are shown in Table 2.7. The peaks obtained for each herbicide were asymmetrical and within the < 2

tailing factor guidelines. The peak area is therefore easier to quantify which contributes to the earlier precision results. The theoretical plate number is a measure of column efficiency. The values obtained from the chromatograph are greater than 2000 for each herbicide.

Table 2.7: Accuracy, capacity factor, tailing factor and theoretical plate values calculated for 0.6 mmol/L MCPA, 2,4-D and dichlorprop chromatograph peaks.

Herbicide	Accuracy (%)	Capacity factor	Tailing factor	Theoretical plates
MCPA	101	0.7	1.7	2792
2,4-D	99	0.7	1.5	2294
dichlorprop	100	1.0	1.4	2771

2.4 Conclusion

A reverse phase high performance liquid chromatography method was developed for the detection and quantitation of MCPA, 2,4-D and dichlorprop. The method was based on a reverse phase system with a methanol/water mobile phase and a C18 bonded silica column. Although initial method development focused on a gradient method for multiple herbicide analysis, the method did not provide satisfactory separation of 2,4-D and MCPA. Therefore, an isocratic method for single component analysis was deemed appropriate and further developed and validated. Method validation was applied to prove that the technique was suitable for the purpose of quantifying herbicide in an aqueous and organic sample. The method was deemed to be precise and accurate. Results remained linear over a wide range from 0.01 mmol/L to 1 mmol/L. The method is suitable to quantify herbicide concentrations in aqueous and organic samples This is required for future chapters were herbicides are removed from water by activated carbon adsorption and liquid-core microcapsule perstraction.

Chapter 3

Removal of chlorophenoxy herbicides from water using activated carbon types typically used in the drinking water treatment process: Comparing the activated carbon and the effect of pH

3.1 Introduction

In the present study, the adsorption capacity of four commercial activated carbons have been examined for the removal of three chlorophenoxy herbicides from aqueous solution. The adsorption equilibrium isotherms have been fitted to the Langmuir and Freundlich isotherm models. The model calculated adsorption capacity has been used to compare two granular activated carbons (AquaSorb 2000 and Norit 1240W) to a powdered (BP2 ColorSorb) and a standard grade laboratory (Sigma Aldrich C-3014) activated carbon. Adsorption of chlorophenoxy herbicides has been previously studied in the literature over a pH range from 2 to 12 to determine the effect on the adsorption process. Typically, as pH increases, adsorption decreases and is most favourable when pH = pk_a of the adsorbate [78, 79, 80, 81, 82]. MCPA, 2,4-D and dichlorprop are acidic and would require a pH range between 2 and 3 for the most favourable adsorption to occur. These pH values would be unsuitable for a drinking water treatment plant as vital plant equipment would be subject to corrosion. Therefore, the present study looks at the pH conditions encountered in drinking water treatment by altering the pH of the solution from an unbuffered system to a pH 4, 6 and 8 pH buffered environment.

3.2 Materials and methods

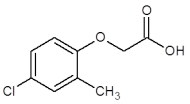
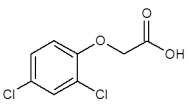
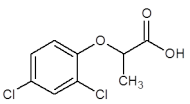
3.2.1 Chemicals

MCPA, 2,4-D and dichlorprop were used as described in Section 2.2.1, page 52. HPLC grade water and methanol were purchased from Fisher Scientific (Dublin, Ireland).Reagent grade citric acid, trisodium citrate, sodium phosphate monobasic, sodium phosphate dibasic and formic acid (mass spectrometry grade) were purchased from Sigma Aldrich (Dublin, Ireland).

Herbicide stock solutions were prepared in methanol and then serially diluted to obtain the desired working concentrations in ultrapure water, which contained maximum final

methanol concentrations between 1 and 6 % (v/v). For experiments where the pH of herbicide solutions was controlled, the ultrapure water (Milipore) contained a buffer reagent. Buffers were prepared by combining either 0.1 M citric acid and trisodium citrate (pH 4 and 6) or sodium phosphate monobasic and sodium phosphate dibasic (pH 8).

Table 3.1: Herbicide specifications

Parameter	MCPA	2,4–D	dichlorprop
formulae	$C_9H_9ClO_3$	$C_8H_6Cl_2O_3$	$C_9H_8Cl_2O_3$
molecular weight (Da)	200.6	221.0	235.1
solubility in water (mg/L)	734 (25 °C)	311 (25 °C, pH 1)	350 (20 °C)
pKa	3.07	2.64	3.00
structure			

3.2.2 Activated carbons

Three granular activated carbon types (AquaSorb 2000, Norit 1240W and Sigma Aldrich C-3014) and one powdered activated carbon (BP2 ColorSorb) were used in this study. ENVA Water Treatment (Cork, Ireland) donated AquaSorb 2000 GAC and BP2 ColorSorb PAC manufactured from bituminous coal by Jacobi Carbons (Kalmar, Sweden). Northern Ireland Water (Belfast, Northern Ireland) donated Norit 1240W GAC produced from coal by Norit (Amersfoort, The Netherlands). Untreated GAC produced from peat bog (Sigma Aldrich C-3014) was used for comparison purposes.

The information supplied by the AC manufacturers [83, 84, 85, 86] is listed in Table 3.2. However, as the Sigma Aldrich C-3014 is an untreated standard laboratory grade AC, the information on the specifications are limited. Norit 1240W and AquaSorb 2000 are produced by different manufacturers but both present similar specifications such as particle size (0.425-1.70 mm), iodine number (>1000) and moisture content (<5 wt %). By comparison, BP2 ColorSorb has a smaller particle size (0.045-0.15 mm) and a smaller surface area (950 m^2/g). Sigma Aldrich C-3014 has the largest particle size (0.84-2.4 mm) but also

the smallest surface area (600-800 m^2). These specifications reflect the difference between highly specialised activated carbons used in DWTPs and the general activated carbons used in laboratories for non-specific applications.

Norit 1240W and AquaSorb 2000 activated carbons are currently implemented in drinking water treatment plants by Northern Ireland Water and ENVA Ireland, respectively. Typical applications for Norit 1240W and AquaSorb 2000 include water treatment and industrial liquid processes. BP2 ColorSorb (Jacobi) is a powdered activated carbon primarily used in process treatment in chemical, food and pharmaceutical industries, to remove colour and adsorb low concentrations of medium to high molecular weight contaminants. Although the application of GAC in flow through systems differs from the dosing and slurries attributed to PAC usage, both can be effectively used to remove hazardous organic pollutants such as herbicides in drinking water treatment plants. Therefore the comparison in this study is a valuable comparison of GAC and PAC abilities under identical conditions. In addition to this comparison, an untreated standard laboratory activated carbon sold by Aldrich was used to evaluate and compare the effectiveness of commercially available high specification activated carbons used in water purification.

Table 3.2: Manufacturers specifications for AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons.

Properties	AquaSorb 2000	Norit 1240W	BP2 ColorSorb	Sigma Aldrich C-3014
surface area (m^2/g)	1050	1150	950	600-800
particle size (mm)	0.425 -1.70	0.425-1.70	0.045-0.15	0.84-2.4
iodine number (mg/g)	$>$1000	$>$1000	$>$850	-
pore volume (cm^3/g)	1.04	-	1.56	-
moisture content (wt%)	$<$5	$<$5	$<$8	-
shape	granular	granular	powder	granular
pH	8-11	alkaline	7-9	9-11

3.2.3 Experimental

Equilibrium loadings of the selected herbicides were obtained by contacting duplicate samples containing 50 mg of each activated carbon with 100 mL of herbicide concentrations (0.1 - 0.6 mmol/L). The aqueous phase was ultra-pure water unless otherwise stated and pH adjustment was carried out as described in section 3.2.1. Control samples were prepared and treated in the same manner, excluding the addition of activated carbon. Suspensions were shaken on a gyratory shaker (model G10, New Brunswick Scientific Co, Inc, Edison, N.J.) at 150 RPM overnight (15 hours) in the dark at 10 °C. Equilibrium concentrations were filtered through a 0.2 μm nylon syringe filter (Phenomenex, Cheshire, United Kingdom) to remove any trace of activated carbon. Initial and equilibrium herbicide concentrations were determined by HPLC.

3.2.4 Detection method

HPLC analysis was performed as previously described in Section 2.2.2, page 53. External standards accompanied each sample set to ensure accurate results. The quantification of the herbicides was based on the external standards method using chromatogram peak areas. For standard calibrations, a linear regression (R^2) value of at least 0.999 was obtained.

3.2.5 Data analysis

Adsorption isotherm model parameters were evaluated by non-linear regression using Datafit software (Oakdale Engineering, USA). Equilibrium models were used to describe the equilibrium between MCPA, 2,4-D and dichlorprop and the selected activated carbons at constant temperature at pH 4, 6 and 8. Adsorption at equilibrium, q (mmol/g), was calculated by:

$$q = (C_i - C_e)\frac{V}{W} \tag{3.1}$$

Where, q is the equilibrium amount of herbicide on the adsorbent (mmol/g) , C_i is the initial herbicide concentration (mmol/L), C_e is the equilibrium herbicide concentration (mmol/L), V is the volume of the solution (L) and W is the weight of the adsorbent (g) .

The Langmuir isotherm model (1.1) and Freundlich isotherm model (1.3) were applied as described in 1.4.3, page 41. Apart from the regression coefficient (R^2), residual sum of squares (SSE) and standard error of estimates (SE) were also used to evaluate the accuracy of the calculated results. The residual sum of squares (SSE) can be defined as:

$$SSE = \sum_{i-1}^{m} (Q_i - q_i)^2 \tag{3.2}$$

The standard error of estimates (SE) can be defined as:

$$SE = \sqrt{\frac{1}{m-p} \sum_{i-1}^{m} (Q_i - q_i)^2} \tag{3.3}$$

where, q_i is the observation from the batch experiment i, Q_i is the estimate from the isotherm for corresponding q_i, m is the number of observations in the experimental isotherm and p is number of parameters in the regression model where the smaller SE and SSE values indicate the best curve fit. In the present study, the correlation coefficient, R^2, SE and SSE values were used to determine the best fit model [87].

3.3 Results and discussion

3.3.1 Initial pH experiments

Adsorption isotherms from aqueous solutions were initially obtained using 0.05 g AquaSorb 2000 and 50 mL MCPA solutions at concentrations ranging from 0.2 - 0.6 mmol/L. These solutions were initially unbuffered and the initial pH varied from 3.41 - 3.82 (depending on

herbicide concentration). The pH changed to 5.26 - 6.03 after MCPA was adsorbed to the activated carbon. The experiment was then repeated using a pH 4 citric buffer (as described in section 3.2.1) and compared to samples which were manually adjusted to pH 4 with NaOH.

Figure 3.1 shows decreased adsorption when the solution pH was controlled by NaOH addition. The solution pH values recorded during this experiment before activated carbon was added and after equilibrium are shown in Table 3.3. No pH change was observed for buffered solutions or the controls containing no activated carbon. However, the samples which were adjusted to pH 4 by NaOH addition did not maintain a pH of 4. The final equilibrium pH observed ranged between pH 6.01 and 6.89.

Table 3.3: Solution pH values for MCPA on AquaSorb 2000 before activated carbon addition and after equilibrium adsorption for control and experimental samples at pH 4 (buffered) and pH 4[a] (unbuffered and adjusted with NaOH).

sample	concentration (mmol/L)	pH before AC addition	pH at equilibrium
pH 4	0.2	4.03	4.07
pH 4	0.3	4.06	4.10
pH 4	0.4	4.08	4.13
pH 4	0.5	4.11	4.15
pH 4	0.6	4.14	4.18
pH 4 control	0.2	4.01	4.08
pH 4 control	0.3	4.05	4.09
pH 4 control	0.4	4.03	4.07
pH 4 control	0.5	4.03	4.07
pH 4 control	0.6	4.05	4.12
pH 4[a]	0.2	4.04	6.01
pH 4[a]	0.3	4.06	6.55
pH 4[a]	0.4	4.01	6.59
pH 4[a]	0.5	4.01	6.97
pH 4[a]	0.6	4.01	6.89
pH 4[a] control	0.2	4.01	4.08
pH 4[a] control	0.3	4.05	4.09
pH 4[a] control	0.4	4.03	4.07
pH 4[a] control	0.5	4.03	4.07
pH 4[a] control	0.6	4.05	4.12

Control samples containing no activated carbon maintained the same pH throughout the experiments. The change of pH observed in samples containing activated carbon was depen-

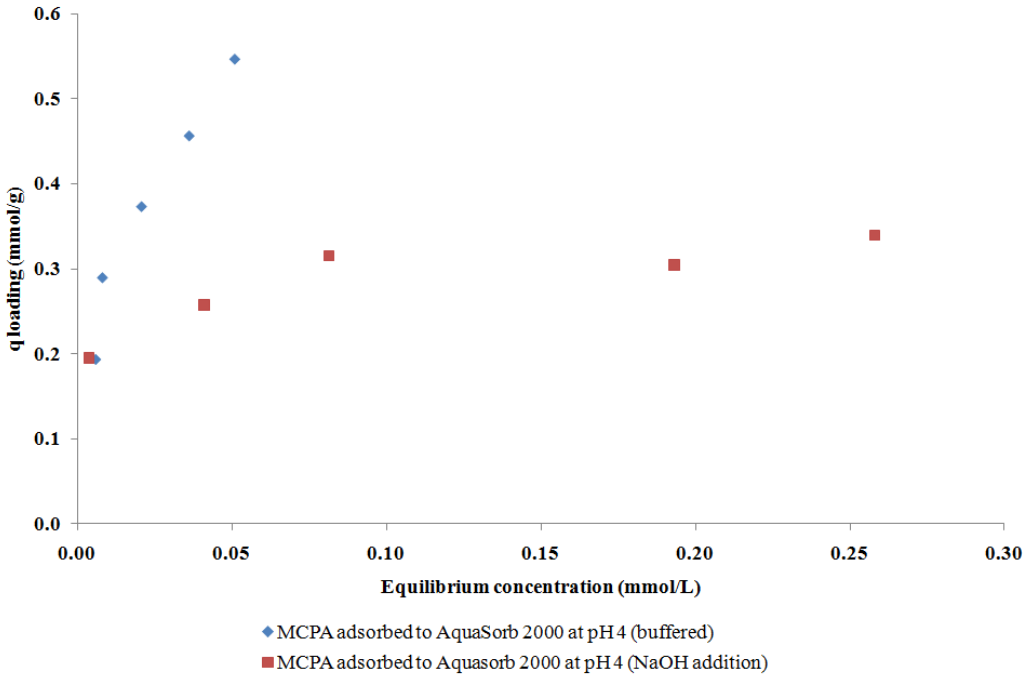


Figure 3.1: Initial pH experiments for MCPA on AquaSorb 2000 at pH 4 (buffered) and NaOH addition.

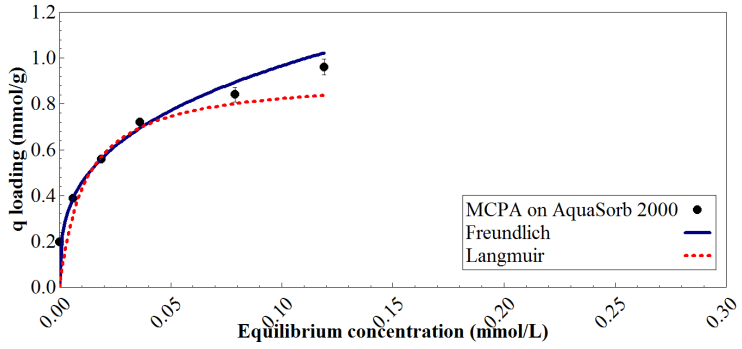
dent on initial herbicide concentration as more acidic herbicide was removed from solution at lower concentrations. This pH change is problematic and leaves the direct comparison of the activated carbons unclear. Following these results, subsequent experiments were performed in unbuffered water and water buffered to pH 4, 6 and 8 as described in 3.2.1.

3.3.2 Equilibrium modelling

The experimental data obtained for MCPA, 2,4-D and dichlorprop on AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 fitted a type I isotherm profile which describes monolayer adsorption [88]. The adsorption results are plotted in Figure 3.2 - 3.5 and exhibit a type I isotherm profile, describing monolayer adsorption. According to the classification by Giles et al [89] the isotherms are classified as L and H type curves. L-shape isotherms show that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites. H-shape isotherms occur when the adsorbate has a high affinity for the adsorbent.

Two frequently used models to describe adsorption for dilute liquid-solid phase systems are the Langmuir and Freundlich isotherms. As described in section 3.2.5 the Langmuir isotherm is based on the assumption of a homogeneous adsorbent with a finite number of adsorption sites which are identical and energetically equivalent. Upon saturation of a monolayer, no more adsorption can take place and the isotherm model plateaus. The Freundlich isotherm is based on a monolayer adsorption principle with a heterogeneous energy distribution of active sites. Both isotherm models contain parameters describing the binding affinity and energy of the adsorbate on the adsorbent, indicating favourable or less favourable adsorption.

Both models were applied to the experimental data to compare the adsorption capacity of the four adsorbents tested. An example of the applied models is given in Figure 3.2 - 3.5 for MCPA adsorption on AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 . Further adsorption isotherm model graphs for 2,4-D and dichlorprop are depicted in Appendix Figure B.1 - B.8. The calculated parameters for both Langmuir and Freundlich isotherms (including R^2, SSE and SE values) are listed in Appendix table B.1 - B.6. The Freundlich model appeared to provide the best fit to the experimental data. The adsorption intensity (n) was favourable in all cases but as values for n remained in the range between 2 and 10, the adsorption process did not become irreversible.



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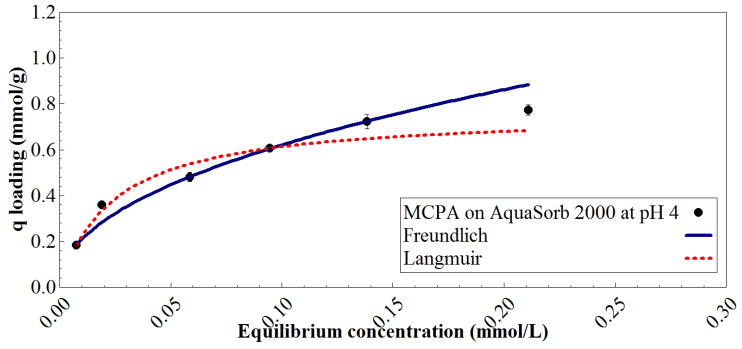

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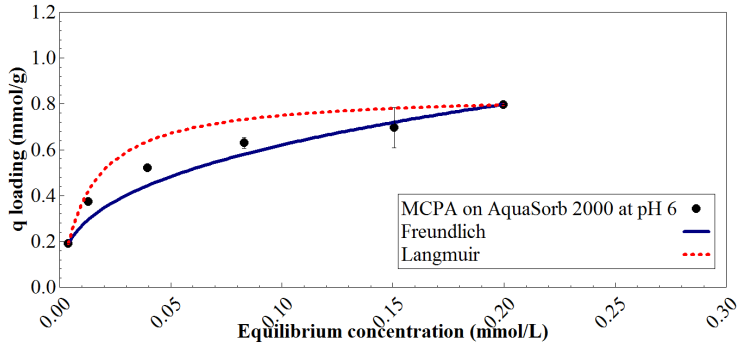

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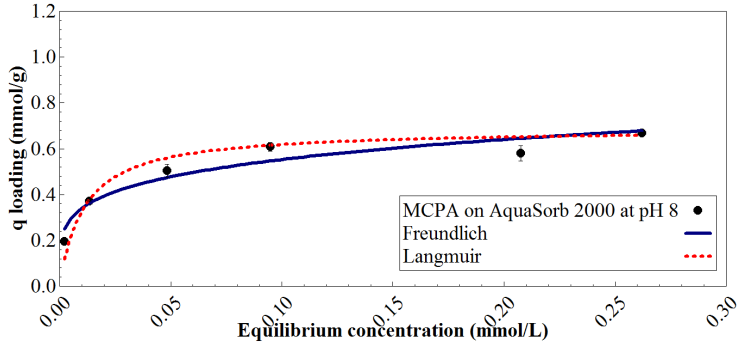
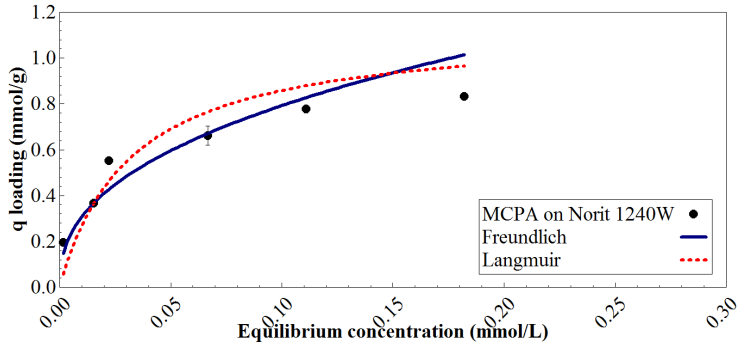


(d)

Figure 3.2: Freundlich and Langmuir isotherm model fit for MCPA adsorption to AquaSorb 2000: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8.



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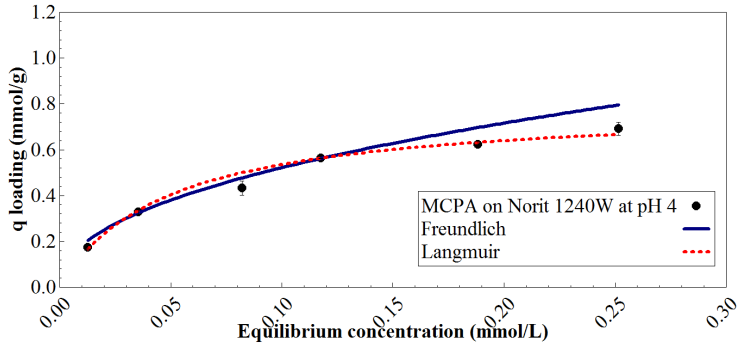

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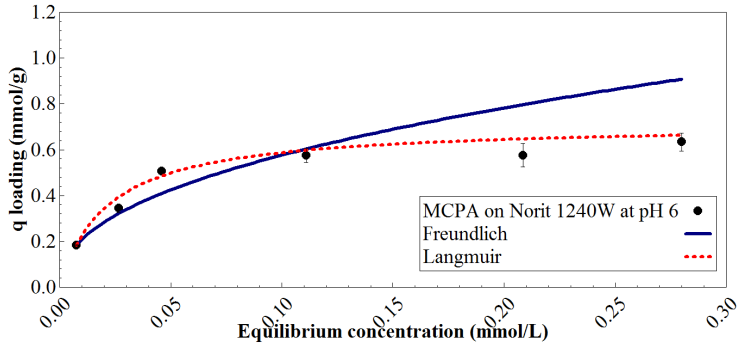

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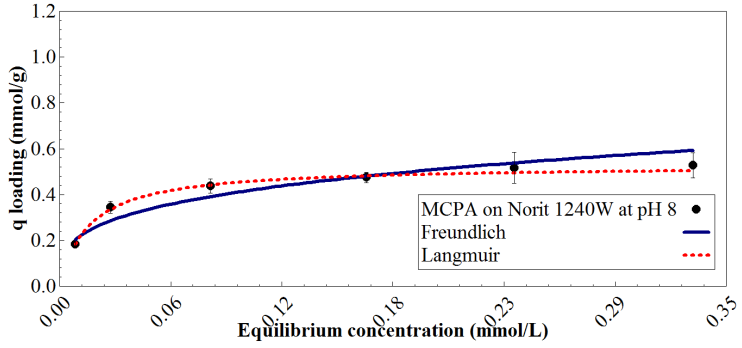
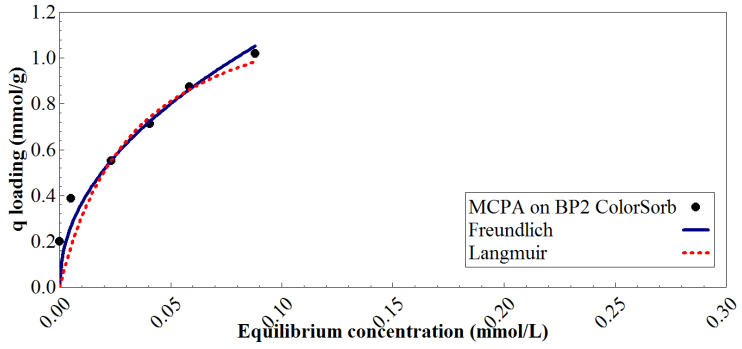


(d)

Figure 3.3: Freundlich and Langmuir isotherm model fit for MCPA adsorption to Norit 1240W: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8.

It was expected that the Sigma Aldrich C-3014 would exhibit the lowest adsorption capacity for the herbicides based on its application as a standard laboratory grade activated carbon with the largest particle size and the smallest surface area. With the exception of pH 8, BP2 ColorSorb shows the highest adsorption capacity. However it must be noted that neither isotherms were a good fit for the experimental data, especially at the higher pH values. The isotherm shapes exhibit a type H curve where the solute has a high affinity and at dilute concentrations it is completely adsorbed, leading to an initial vertical isotherm (Figure 3.4 (d)).

The change in pH from unbuffered solution to controlled pH conditions at pH 6 was unfavourable for BP2 ColorSorb with 2,4-D. Instead, Norit 1240W and AquaSorb 2000 performed better at higher pH values. The adsorption capacity for AquaSorb 2000 with dichlorprop increased as the pH changed from the unbuffered solution to pH 4 and then pH 6 and 8. The adsorption for each herbicide at pH 8 always followed the order of AquaSorb 2000 $>$ Norit 1240W $>$ BP2 ColorSorb $>$ Sigma Aldrich C-3014. It is important to note that AquaSorb 2000 and Norit 1240W have identical properties in terms of iodine number, particle size, shape (granular) and moisture content. Although Norit has the larger surface area, (1150 m^2/g compared to 1050 m^2/g for AquaSorb 2000), with the exception of 2,4-D adsorption at pH 6, its adsorption capacity for the selected herbicides is lower than AquaSorb 2000.



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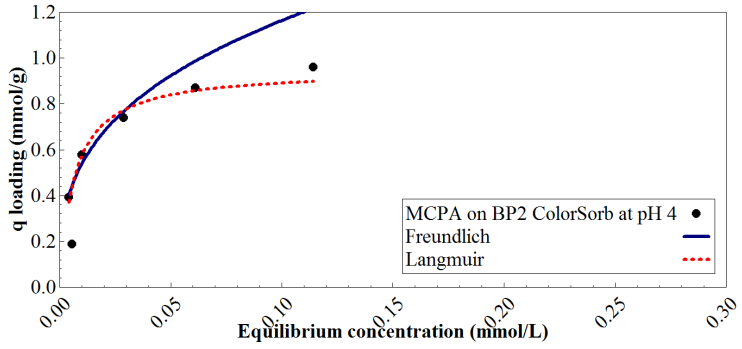

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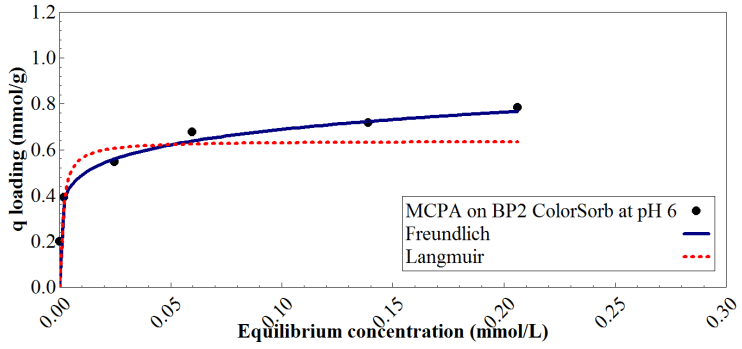

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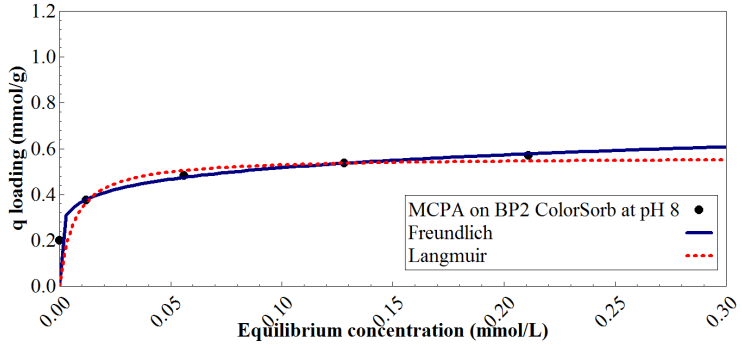
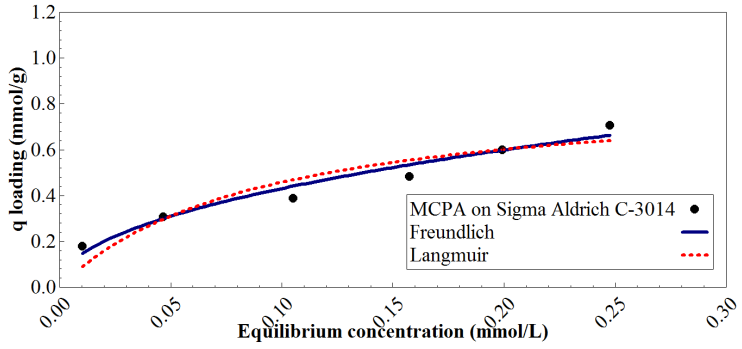


(d)

Figure 3.4: Freundlich and Langmuir isotherm model fit for MCPA adsorption to BP2 ColorSorb: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8.



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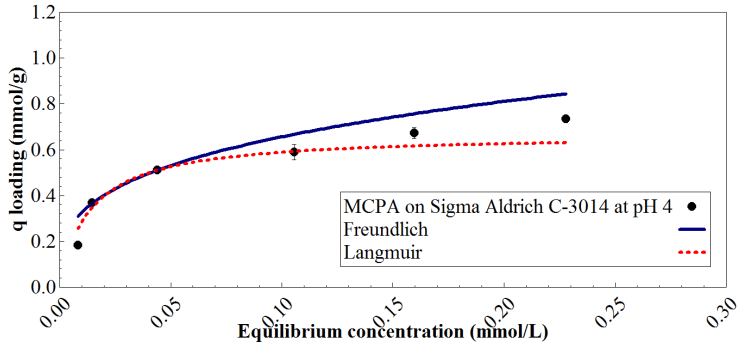

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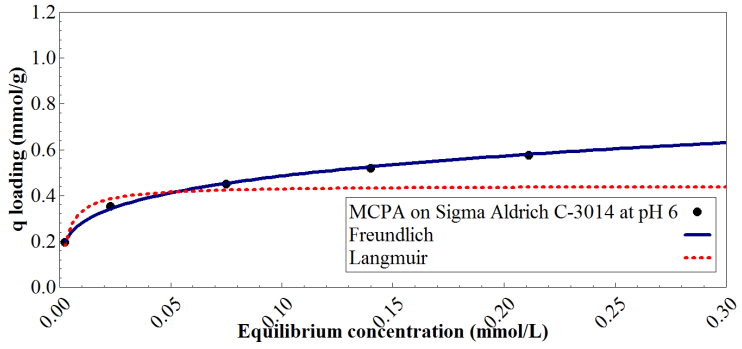
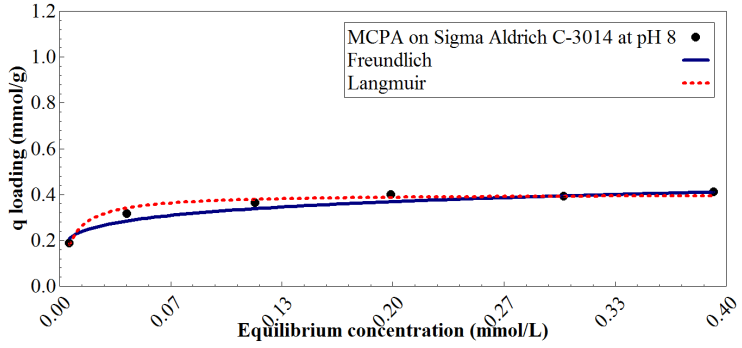


(c)



(d)

Figure 3.5: Freundlich and Langmuir isotherm model fit for MCPA adsorption to Sigma Aldrich C-3014: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8.

3.3.3 Effect of solution pH on herbicide adsorption

The adsorption capacity of activated carbon is dependent on a variety of factors [90, 91], such as:

1. Characteristics of the adsorbent - surface area, pore size distribution and functional groups.
2. Characteristics of the adsorbate - molecular weight and size, functional groups, solubility, polarity, hydrophobicity and pk_a.
3. Solution conditions - temperature, pH, polarity of solvents, presence of competitive solutes and adsorbate concentration.

Therefore this part of the study concentrates on solution conditions, in particular the effect of pH change in a single component system at a constant temperature. The effect of varying the pH relates to the degree of ionization of the adsorbate, the speciation of the adsorbate and the surface charge of the adsorbent. Adsorption to activated carbon for 2,4-D has been found to decrease with increasing pH [79, 80] and maximum adsorption occurs when the pH of the solution is equal to the pk_a value of the herbicide [81].

The design of drinking water treatment plants ensures that activated carbon filters are utilised as tertiary treatment to primarily remove taste and odour and to a lesser extent the removal of pollutants. The pH of water entering a treatment plant is dependent on its location and the environment the water has previously passed through. The water is manually adjusted throughout the plant to a desired pH. Due to this set-up the water at the activated carbon filters is already at a pH between 6 and 8. To facilitate potential values representing a drinking water treatment plant, the pH study in this work concentrates on pH values of 6 and 8. Although it is not feasible in a water treatment plant, pH 4 is included as an acidic parameter. Solutions were controlled by buffer addition as described in section 3.2.1. Results for unbuffered samples were also included for comparison but as described in section 3.3.1 the pH of these samples was not kept constant and varied depending on initial and

equilibrium herbicide concentrations.

The adsorption capacity results for the Freundlich isotherm described in section 3.3.2 were used to evaluate the effect of pH on the adsorption process. The results of the pH study indicate that the change in pH effects the surface of the activated carbon, the degree of ionisation and the interaction between the herbicides and the activated carbon. The change in pH from 4 to 6 for MCPA on AquaSorb 2000 shows (Table B.1, Figure 3.2) a 23 % decrease in adsorption capacity. A further increase in pH from 6 to 8 decreased the capacity by a further 37 %. Similar results were recorded for Sigma Aldrich C-3014 for the same range (37 % and 43 %, respectively). The change in pH from 4 to 6 had the least effect on Norit 1240W (7 %) and the biggest effect on BP2 ColorSorb (61 %).

The pH change between 4 and 6 showed the biggest decrease in adsorption capacity for 2,4-D (Table B.3, Figure B.2) on Norit 1240W (47 %). This decrease is 40 % higher than for MCPA on the same activated carbon under the same conditions. Observed changes in herbicide uptake are most likely due to the characteristics of the herbicide and the interaction between the herbicide and carbon surface. A further increase in pH from 6 to 8, lowered the adsorption capacity by a further 42 %.

The change in pH had a minimal effect on the adsorption of dichlorprop (Table B.5) to Norit 1240W (Figure B.6) and Sigma Aldrich C-3014 (Figure B.8. Adsorption in the case of Norit 1240W increased by 1 % from pH 4 to 6 and then decreased by 10 % between pH 6 and 8. Similar results were observed for Sigma Aldrich C-3014 whereby adsorption increased by 1 % between pH 4 and 6 and then decreased by 32 % between pH 6 and 8.

Decreases in adsorption capacity could be explained by the nature of the herbicides under investigation. MCPA, 2,4-D and dichlorprop are weak acids whereby an increase in pH increases the quantity of ionised molecules which are unfavourably adsorbed compared to the protonated molecules [78, 82]. Deprotonation of the carboxyl group is responsible for the increase in ionised species which are present at pH 4 at quantities of 88 %, 96 % and 90 % for MCPA (pk$_a$ 3.07), 2,4-D (pk$_a$ 2.64) and dichlorprop (pk$_a$ 3.00) respectively. As the pH approaches 6 and 8 the ionisation is almost 100 %. Therefore the pH change controls the electrostatic interactions between the adsorbent and the adsorbate. The solution pH also

effects the surface charge on the activated carbon surface. As detailed in Table 3.2, the activated carbons in this study are basic. Therefore, at pH values equal to the pH value of the activated carbon, the surface carbon is neutral. At higher values, the surface charge is negative and at lower values the surface charge is positive [92]. Thus at lower pH values less ionised species are present and dispersion interactions with the positive carbon surface dominate [93].

3.4 Conclusions

Activated carbon is a widely used in water purification. In drinking water treatment plants it is used as a tertiary method to remove taste, odour and pollutants. However, periodic failures, which cannot be predicted, occur and therefore the aim of this study was to compare the efficiency of commercially activated carbons on the removal of three similarly structured herbicides, which are frequently detected in drinking water, under pH controlled conditions. The conclusions of this work are as follows; Initial pH experiments showed variations in solution pH after activated carbon addition and final equilibrium after 15 hours. Controlling the pH by NaOH addition was not successful and decreased the adsorption capacity of AquaSorb 2000.

Adsorption was controlled by pH and the activated carbon adsorption capacity decreased as pH increased. Adsorption was controlled by the dissociation of MCPA, 2,4-D and dichlorprop and the surface chemistry of the activated carbons. Isotherm data was fitted to both Langmuir and Freundlich models and although both gave good correlation, Freundlich provided a better fit. Adsorption intensity parameters for both showed that the adsorption was a favourable process for each herbicide on all four activated carbons investigated.

Results at pH 8 for each herbicide followed the order of AquaSorb 2000 $>$ Norit 1240W $>$ BP2 ColorSorb $>$ Sigma Aldrich C-3014. AquaSorb 2000 was the best granular activated carbon for removal of chlorophenoxy herbicides across a pH range from 4-8.

Chapter 4

Studying the effect and interference of humic acid addition on the activated carbon adsorption process

4.1 Introduction

NOM is a complex matrix of organic compounds present in natural waters. Humic substances (HS) are high molecular weight components of NOMs and are comprised of hydrophobic and hydrophilic fractions. These factions vary in colour from yellow to black and are responsible for discoloured water. HS can be classified [94] based on their solubility under acidic and basic conditions. Humin is the insoluble HS fraction, humic acid (HA) is the faction only soluble under alkaline conditions and fulvic acid (FA) is the faction soluble under all pH conditions. An example of the Steelink model of a humic acid monomer [95] is shown in Figure 4.1.

HS account for between one third and one half of the dissolved organic carbon (DOC) in natural water. The lowest concentration can be found in groundwater (0.03 - 0.1 mgC/L) and seawater (0.06 - 0.6 mgC/L). Lakes and rivers contain 0.5 - 4 mgC/L. Wetlands such as bogs, marshlands and swamps contain the highest levels of HS (10 - 30 mgC/L) [96].

HS are capable of organising into micellar structures stabilised by hydrophobic interactions and hydrogen bonds [94, 97]. These supramolecular associations may interfere with drinking water treatment processes as the presence of HS in the aquatic environment can have undesirable side effects. Sunlight absorbing HA form precursors to carcinogenic by-products (trihalomethanes) formed during chlorination [98]. Filtration membranes can be fouled by the presence of NOM controlled by a combination of permeation drag and electrostatic double layer repulsion [99]. Activated carbon adsorption can be influenced by NOM by active site competition [100, 101] and pore blockage [102, 103, 104].

The aim if this chapter is to evaluate the direct and indirect impact of HA addition on the adsorption of MCPA, 2,4-D and dichlorprop to AquaSorb 2000 and Norit 1240W GAC. These results were directly compared to treatment by virgin activated carbon from Chapter 3 and results obtained by directly contacting virgin activated carbon with herbicides in water containing humic acid. The electronic interaction between herbicides and HA was studied by UV-Visible differential spectroscopy and fluorescence spectroscopy.

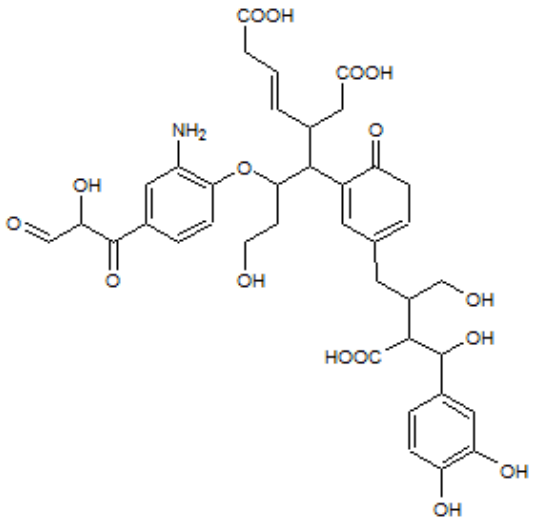


Figure 4.1: The Steelink model of a humic acid monomer [95].

4.2 Materials and methods

4.2.1 Chemicals

Herbicide and regents were used as described in Section 2.2.1, page 52.

Technical grade humic acid sodium salt was purchased from Sigma Aldrich (Dublin,Ireland). The sodium salt product was sourced from decomposed dead plant matter found in vegetable soil, peat and soft coal. The composition includes polysaccharides, proteins, simple phenols and chelated metal ions. The molecular weight was estimated by the manufacturer to be in the range of 2,000 - 500,000 [105]. Humic acid stock solutions were prepared in ultrapure water and filtered through qualitative QL120 (6 μm particle retention) cellulose filter paper (Fisher Scientific, Dublin, Ireland) to remove any remaining particles, followed by serial dilution in ultrapure water to the desired working concentrations.

4.2.2 Activated carbons

AquaSorb 2000 and Norit 1240W granular activated carbon was used as described in Section 3.2.2, page 67.

4.2.3 Experimental

Equilibrium loadings of the selected herbicides were obtained by contacting duplicate samples containing 50 mg of each activated carbon with 10 mL of herbicide concentrations (0.1 - 0.6 mmol/L). Control samples were prepared and treated in the same manner, excluding the addition of activated carbon. Suspensions were shaken on a gyratory shaker (model G10, New Brunswick Scientific Co, Inc, Edison, N.J.) at 150 RPM overnight (15 hours) in the dark at 10 °C. Equilibrium concentrations were filtered through a 0.2 μm nylon syringe filter (Phenomenex, Cheshire, United Kingdom) to remove any trace of activated carbon. Initial and equilibrium herbicide concentrations were determined by HPLC analysis.

4.2.3.1 Humic acid adsorption to activated carbon

Aqueous solutions containing 10 - 100 mg/L humic acid were contacted with 2 g AquaSorb 2000 GAC and Norit 1240W GAC for 15 hours in 200 mL volumes at 150 RPM. Humic acid concentrations were quantified by UV-Visible spectroscopy (LB100 Perkin Elmer, Waltham, MA, USA) at 254nm.

4.2.3.2 Herbicide adsorption in the presence of humic acid

Adsorption isotherms were reproduced as described in 4.2.3 with the addition of 10 - 50 mg/L humic acid to the herbicide solution.

4.2.3.3 Adsorption experiments with activated carbon pre-loaded with humic acid

Adsorption isotherms were reproduced as described in section 4.2.3 using AquaSorb 2000 and Norit 1240W saturated with humic acid (30 mg/L) recovered by filtration from experiments described in 4.2.3.1.

4.2.4 Detection methods

4.2.4.1 High performance liquid chromatography

HPLC analysis was performed as described in Section 2.2.2, page 53.

4.2.4.2 UV-Visible spectroscopy

UV-Visible analysis was performed as described in Section 2.2.2, page 53.

4.2.4.3 Fluorescence spectroscopy

Humic acid and herbicide samples were examined for fluorescence using a Perkin Elmer (Perkin Elmer, Waltham, MA, USA) L550-B scanning spectrofluorometer. The instrument was operated at an excitation and emission slit width of 5 nm. The scanning speed was set to 600 nm/min with a 1 nm data interval. Quartz cuvettes were used to minimise background interferences.

Humic acid sodium salt (10 - 50 mg/L) fluorescence was examined at an excitation wavelength of 330 nm. The emission spectrum was produced between 350 and 650 nm. Herbicide (0.01 - 0.6 mmol/L) fluorescence spectra were obtained between 285 and 370 nm after excitation at 280 nm.

4.2.5 Data analysis

4.2.5.1 Activated carbon equilibrium concentrations

Equilibrium models were used to describe the equilibrium between MCPA, 2,4-D and dichlorprop and the selected activated carbons.

Adsorption at equilibrium, q (mmol/g), was calculated by:

$$q = (C_i - C_e)\frac{V}{W} \tag{4.1}$$

Where, q is the equilibrium amount of herbicide on the adsorbent (mmol/g) , C_i is the initial herbicide concentration (mmol/L), C_e is the equilibrium herbicide concentration (mmol/L) , V is the volume of the solution (L) and W is the weight of the adsorbent (g) .

4.2.5.2 Differential UV-Visible spectroscopy

Differential UV-Visible spectroscopy of humic acid sodium salt after herbicide addition was calculated as follows:

$$\Delta A_\lambda = A_\lambda^m - A_\lambda^h - A_\lambda^{HA} \tag{4.2}$$

In the formula A_λ^m represents the absorbance of the mixture, A_λ^h is the absorbance of the herbicide and A_λ^{HA} is the humic acid absorption at wavelength λ.

4.2.5.3 Stern-Volmer relationship

The Stern-Volmer equation was used to describe the quenching mechanism between the herbicides and increasing HA concentrations.

$$\frac{I^0}{I} = 1 + K_{SV}[Q] \tag{4.3}$$

Where, I^0 and I is the fluorescence intensity in the absence and in the presence of a quencher, respectively. K_{SV} is the Stern-Volmer constant and [Q] is the quencher concentration.

4.2.5.4 Perrin model

The Perrin model describes the proximity of the quencher to the fluorophores in a sphere volume as follows:

$$\frac{I^0}{I} = \frac{4}{3}\pi {R_S}^3 \tag{4.4}$$

Where, R_s is the radius of the quenching sphere. The slope obtained from plotting ln I^0/I vs quencher concentration is equal to R_s according to:

$$\frac{I^0}{I} = \frac{4}{3}\pi {R_S}^3 = slope(HA)[Herbicide] \tag{4.5}$$

4.3 Results and discussion

4.3.1 Humic acid adsorption to activated carbon

Humic acid adsorption to AquaSorb 2000 and Norit 1240W was evaluated by contacting 10-100 mg/L humic acid sodium salt with 2 g activated carbon in 200 mL ultrapure water. Equilibrium samples were measured and quantified by UV-Visible at 254 nm. Maximum removal (49 %) was recorded at the lowest concentration of HA, decreasing as concentration increased. This suggests the AC adsorption capacity is being reached at higher concentrations. Maximum q loading values were 0.9 mg/g for 100 mg/L HA. This suggests that although humic acid is removed by activated carbon, the adsorption process is not very effective.

4.3.2 Competitive adsorption behaviour

Adsorption experiments containing 0.5 mmol/ L herbicide contacted with 50 mg AquaSorb 2000 and Norit 1240W in the presence of 10 - 50 mg/L humic acid were investigated. As humic acid concentration increased, herbicide adsorption decreased. The q loading values for MCPA, 2,4-D and dichlorprop on both ACs with and without HA addition (50 mg/L) are shown in Table 4.1. The decrease in q loading values can be attributed to pore blocking

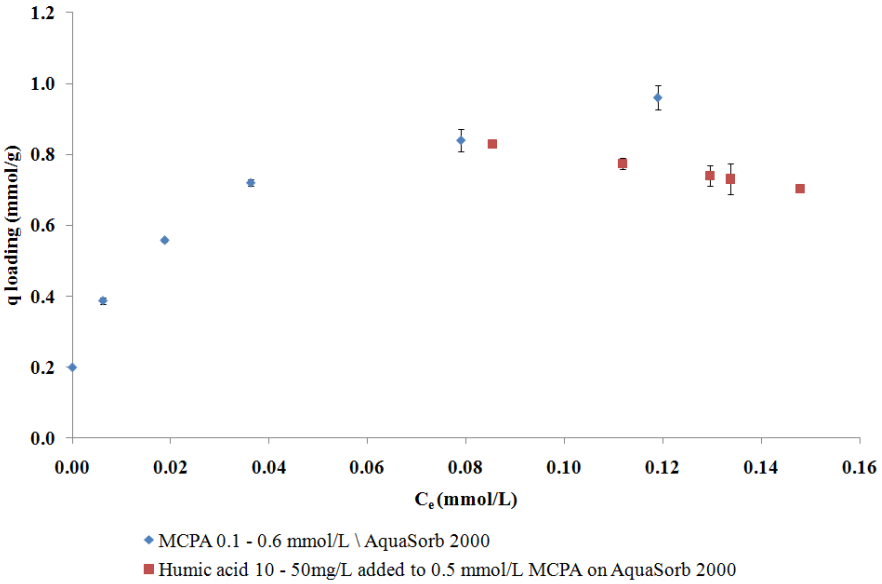


Figure 4.2: Equilibrium q loadings for MCPA (0.1 - 0.6 mmol/L) contacted with virgin Aquasorb 2000 and the effect on 0.5 mmol/L MCPA q loadings by HA addition (10 - 50 mg/L).

mechanisms [102, 103, 106] whereby the larger humic acid molecules are blocking the herbicide from gaining entry to the porous carbon structure. Previous experimental results extrapolated from the data in Section 4.3.1 show that the q loading value for 50mg/L HA on both carbons is 0.7 mg/g. Figure 4.2 compares the decrease in adsorption capacity for MCPA 0.5 mmol/L when 10 - 50 mg/L HA is added to the aqueous phase. The graph shows the concentration dependent decline in adsorption capacity as the concentration of HA is increased.

Table 4.1: Equilibrium q loadings for MCPA, 2,4-D and dichlorprop on AquaSorb 2000 and Norit 1240W comparing the q loadings from virgin AC experiments to the q loadings when 50 mg/L humic acid (HA) was added to the adsorption system.

	AquaSorb 2000		Norit 1240W	
Herbicide	AC q loading	50 mg/L HA	AC q loading	50 mg/L HA
MCPA	0.84 mmol/g	0.70 mmol/g	0.78 mmol/g	0.66 mmol/g
2,4-D	0.87 mmol/g	0.62 mmol/g	0.78 mmol/g	0.55 mmol/g
dichlorprop	0.66 mmol/g	0.57 mmol/g	0.51 mmol/g	0.46 mmol/g

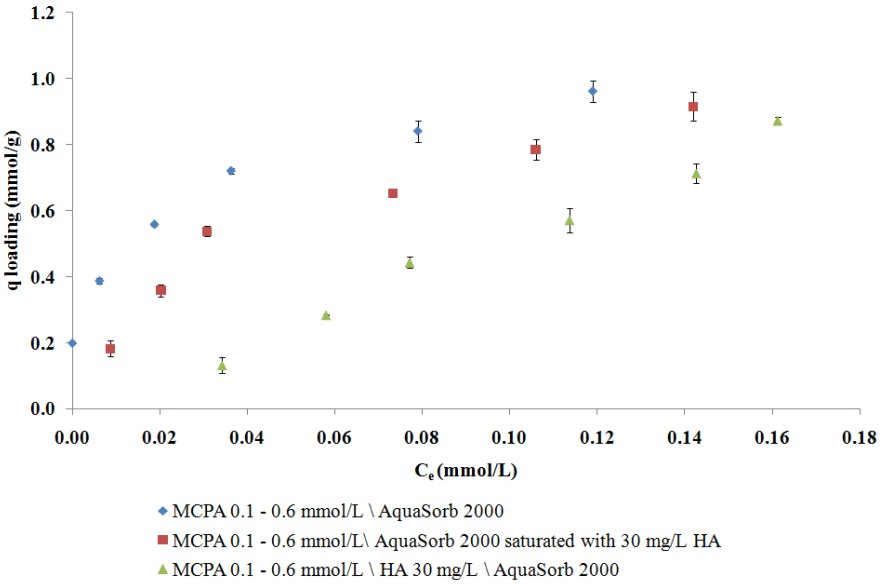


Figure 4.3: Equilibrium q loadings for MCPA (0.1 - 0.6 mmol/L) contacted with virgin AquaSorb 2000, AquaSorb 2000 preloaded with 30 mg/L HA and adsorption when HA 30 mg/L was added to MCPA and virgin AquaSorb 2000.

4.3.3 Herbicide adsorption to humic acid pre-loaded activated carbon

AquaSorb 2000 and Norit 1240W activated carbons were recovered after equilibrium loadings were achieved with a starting concentration of 30 mg/L humic acid. Analysis described in Section 4.3.1 concluded 19 mg/L humic acid remained in solution after equilibrium with 11 mg/L HA adsorbed to 2 g of each activated carbon sample. These activated carbons were then reused once to adsorb each herbicide at a concentration range of 0.1 - 0.5 mmol/L as previously described. MCPA comparison between original herbicide removal, adsorption in the presence of humic acid and adsorption to activated carbon loaded with humic acid are presented in Figure 4.3. The graph shows a greater decline in herbicide uptake in direct competition with humic acid than when the activated carbon was pre-saturated. This suggests an inhibition mechanism is more likely caused by direct competition for adsorption sites rather than pore blockage. Similar results were recorded for 2,4-D and dichlorprop.

4.3.4 Interaction between herbicides and humic acid

The decrease in adsorption capacity and possible site competition or interaction between the herbicides and humic acid is of interest. It is proposed that possible charge transfer interaction could be visible during spectroscopic analysis. Therefore the UV-Visible and fluorescence interactions were investigated.

4.3.4.1 UV-Visible spectroscopic analysis

The UV-Visible spectrum of humic acid has previously been reported as being broad and featureless with a decreasing trend in absorbance values as wavelength increases [107]. The UV-Visible spectrum for humic acid sodium salt used in this study, shown in Figure 4.4 (a) exhibits the same adsorption behaviour as previously cited. The HA spectrum displayed a linear absorption response, as shown in Figure 4.4 (b).

Electronic communication between the herbicides and HA would be evident in significant modifications to the UV-Visible spectroscopy of both. In order to elucidate the presence of any new optical transitions due to electronic interaction, differential UV-Visible spectroscopy was used. A range of solutions were prepared, each containing 30 mg/L HA and a varying quantity of herbicide from 0.1 - 0.6 mmol/L. The lack of distinct features in the HA UV-Visible spectrum (as shown in Figure 4.4) means no one peak can be monitored for change. Therefore the UV-Visible spectrum was scanned from 200 to 470 nm.

Figure 4.8 shows the differential UV-Visible spectrum for MCPA and HA. The data used to construct the differential UV-Visible spectrum was obtained by subtracting the separate UV-Visible signal for MCPA (Figure 4.6) and HA (Figure 4.5) from the UV-Visible spectrum obtained from the mixture solution (Figure 4.7) containing both MCPA and HA according to Equation 4.2. The differential spectrum for 2,4-D (Figure 4.11) was analysed in the same way by subtracting the spectrums in Figures 4.9 and 4.5 from Figure 4.10. Dichlorprop (Figure 4.14) from Figures 4.12 and 4.5 was subtracted from the spectrum in Figure 4.13.

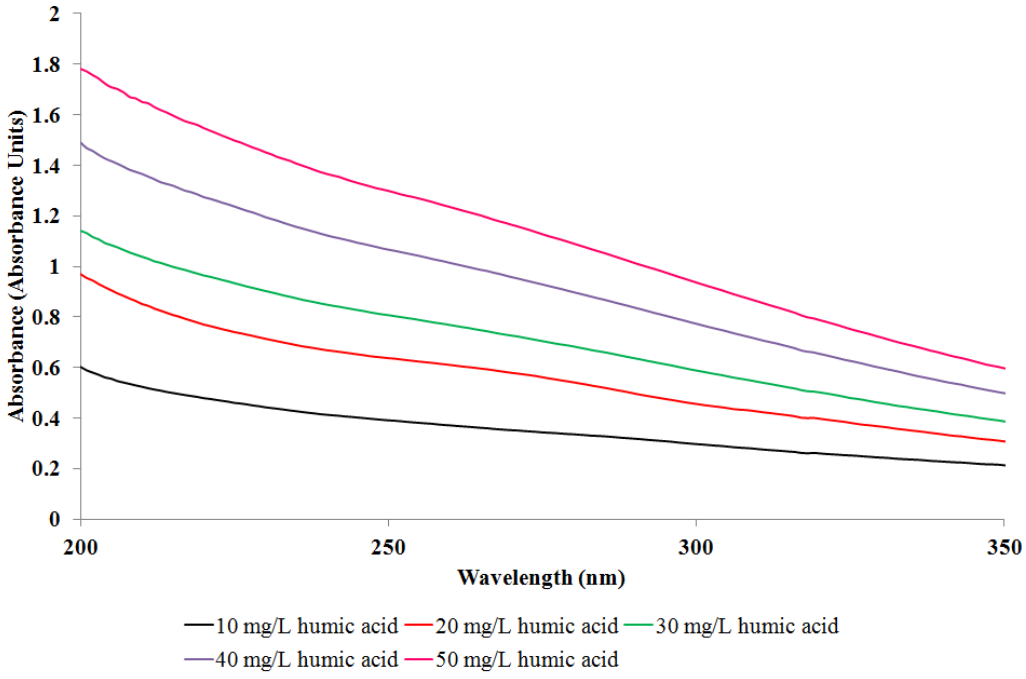
The differential absorbance between 270 - 290 nm for each herbicide mixture shows the presence of a weak new spectral feature. The UV-Visible absorptivity at 280 nm is where π–π^* electron transitions occur for aromatic substances[108, 109]. It is important to note that the spectral change does not appear to depend on concentration changes.

A Jobs plot of the differential adsorption against the molar fraction could determine if this is a true transfer of charge. However, the mole fraction cannot be calculated unless the exact molecular weight of the HA fraction is known. Thus far the concentration of HA has been reported in units of mg/L as the molecular weight from the manufacturer was estimated between 2,000 and 500,000. Further work would need to be carried out to characterise the HA used in the study.

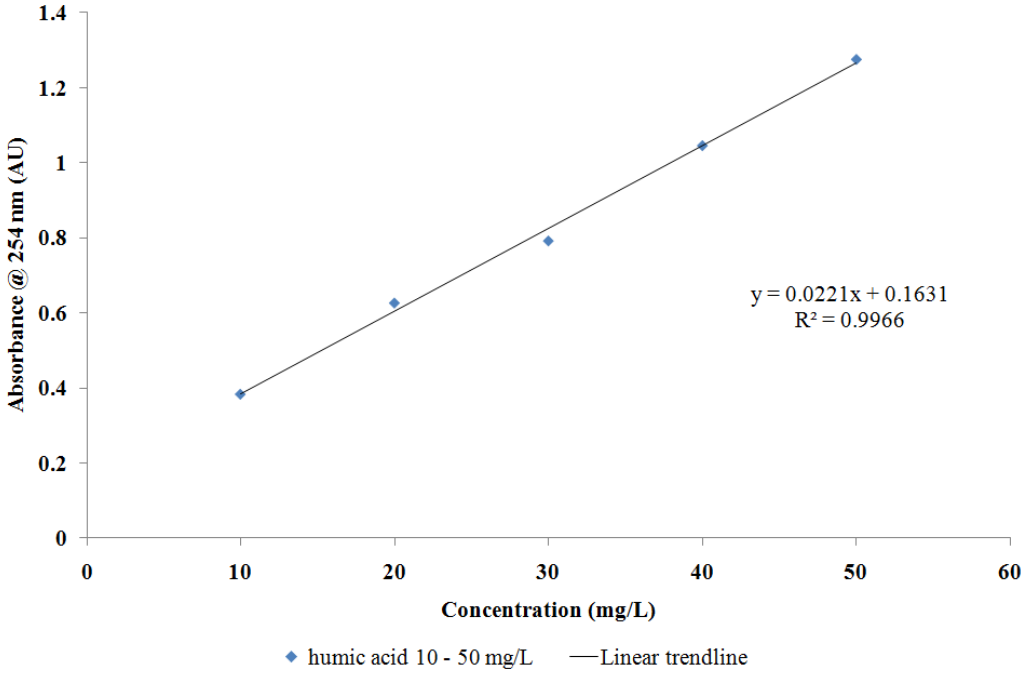
4.3.4.2 Fluorescence spectroscopy

Fluorescence emission from a substance occurs when an electron absorbs electromagnetic radiation and is excited to a higher energy state. A photon of light is emitted when the electron returns to the ground state. The process occurring between the absorption and emission of light is illustrated by the Jablonski diagram (Figure 4.15). Fluorescence measurements can provide information on several molecular processes, such as interactions of solvent molecules with fluorophores, conformational changes and binding interactions.

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. Quenching can occur due to molecular interactions such as excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation and collisional quenching. Quenching can be classified as either static or dynamic (collisional). Dynamic quenching is described by the Stern-Volmer equation (4.3). The data is presented as plots of I^0/I versus [Q] and expected to be linearly dependent on the concentration of the quencher. Linear Stern-Volmer plots result from diffusive encounters between one class of fluorophore and quencher in a time dependent excited state. Static quenching occurs when fluorophore and quencher form a non fluorescent ground-state complex. The complex absorbs light, while immediately returning to the ground state without the emission of a photon. How-



(a)



(b)

Figure 4.4: UV-Visible spectrum (a) and calibration curve (b) for humic acid sodium salt (10 - 50 mg/L.)

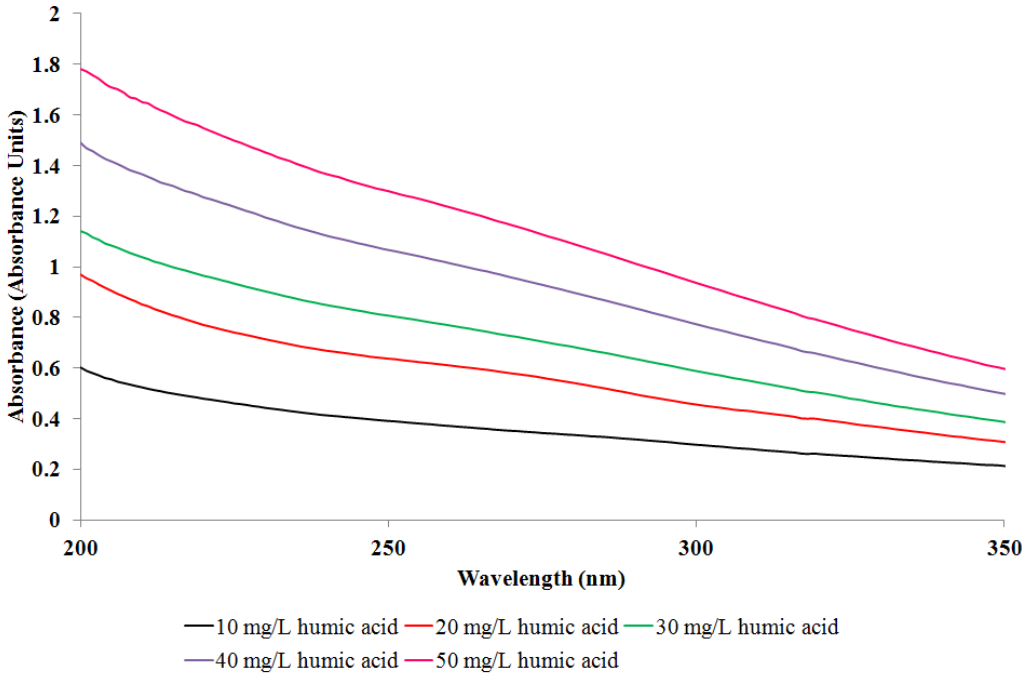


Figure 4.5: UV-Visible spectra for humic acid (10 - 50 mg/L).

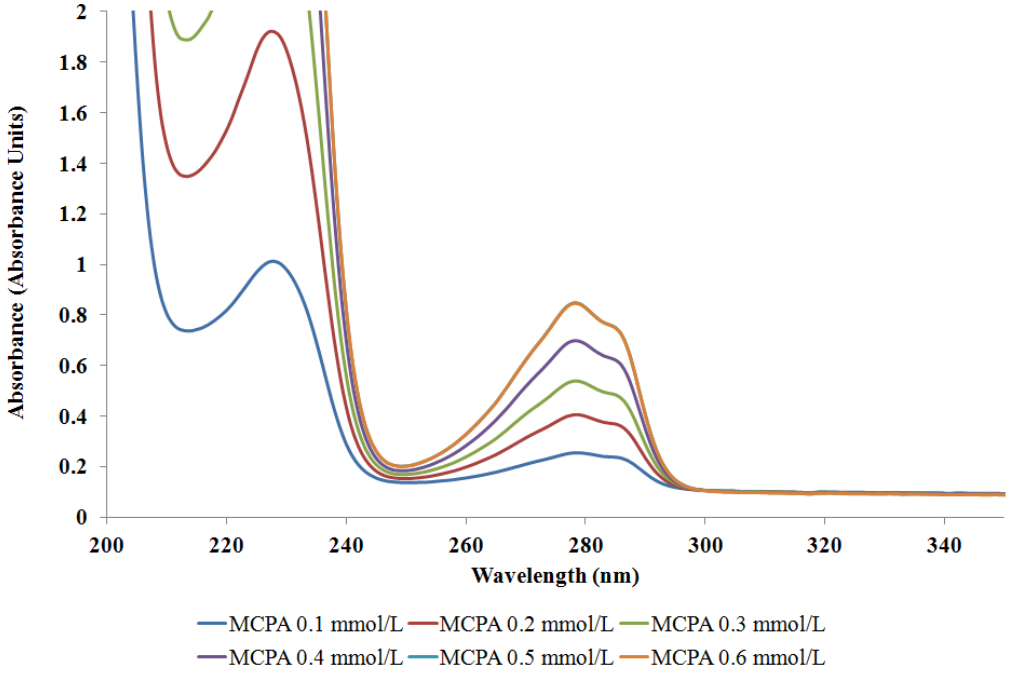


Figure 4.6: UV-Visible spectra for MCPA (0.1 - 0.6 mmol/L).

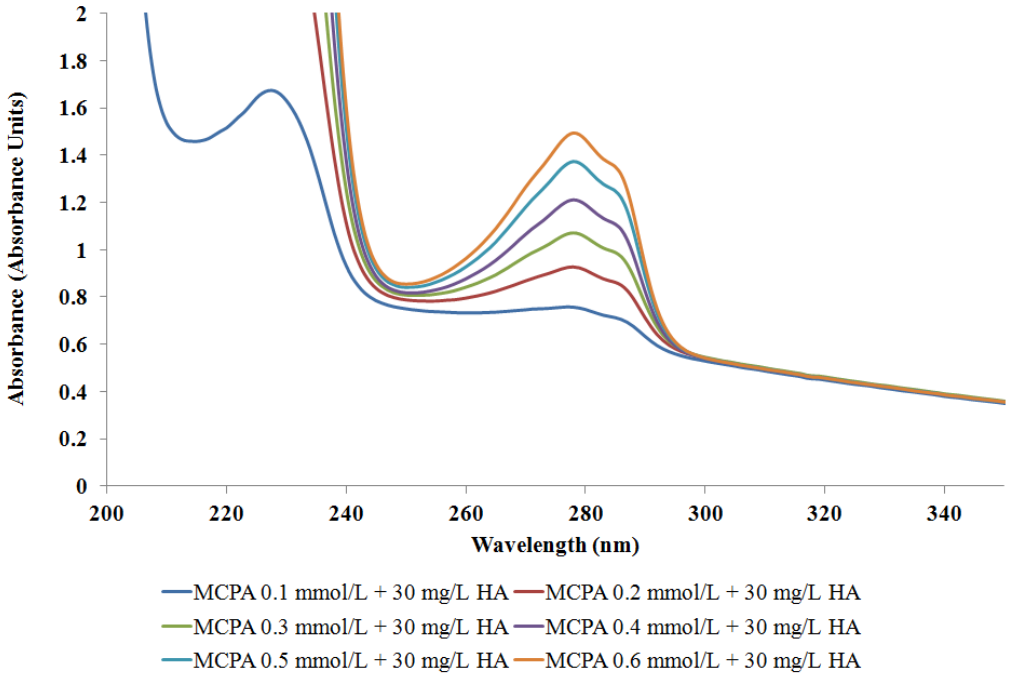


Figure 4.7: UV-Visible spectra for mixtures containing MCPA (0.1 - 0.6 mmol/L) and HA (30 mg/L).

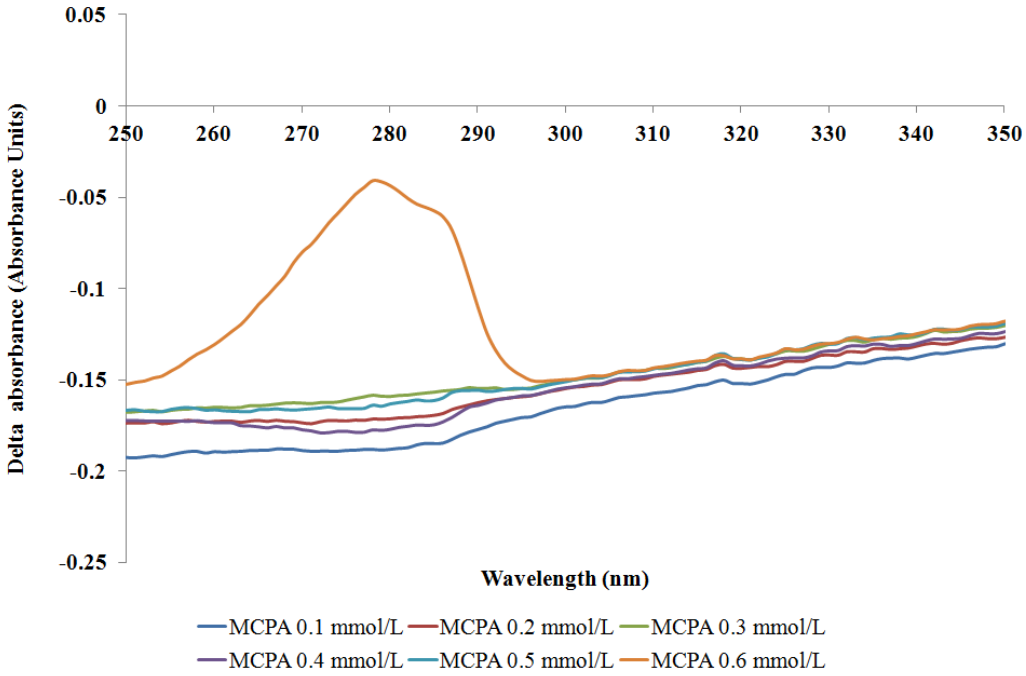


Figure 4.8: UV-Visible differential spectrum obtained from Figure 4.7 which contained MCPA (0.1 - 0.6 mmol/L) and HA (30 mg/L).

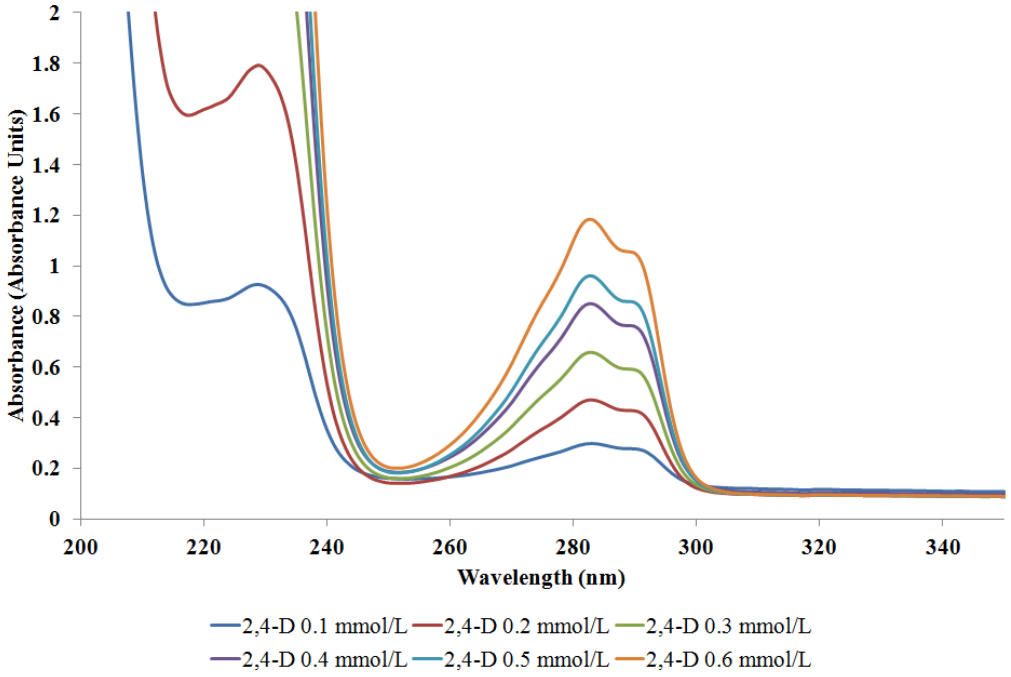


Figure 4.9: UV-Visible spectra for 2,4-D (0.1 - 0.6 mmol/L).

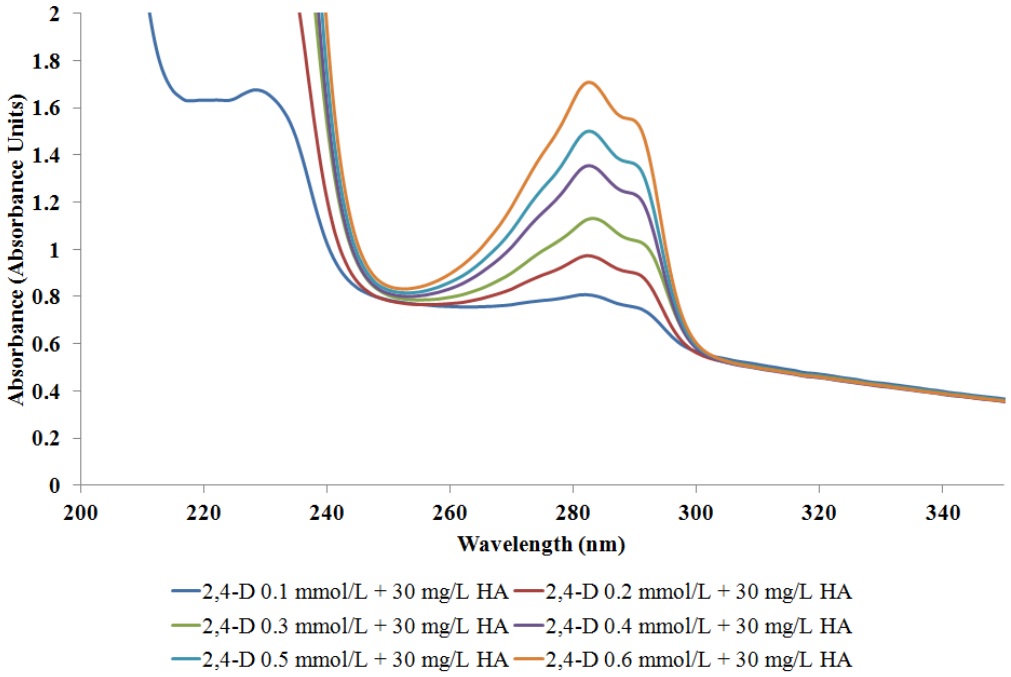


Figure 4.10: UV-Visible spectra for mixtures containing 2,4-D (0.1 - 0.6 mmol/L) and HA (30 mg/L).

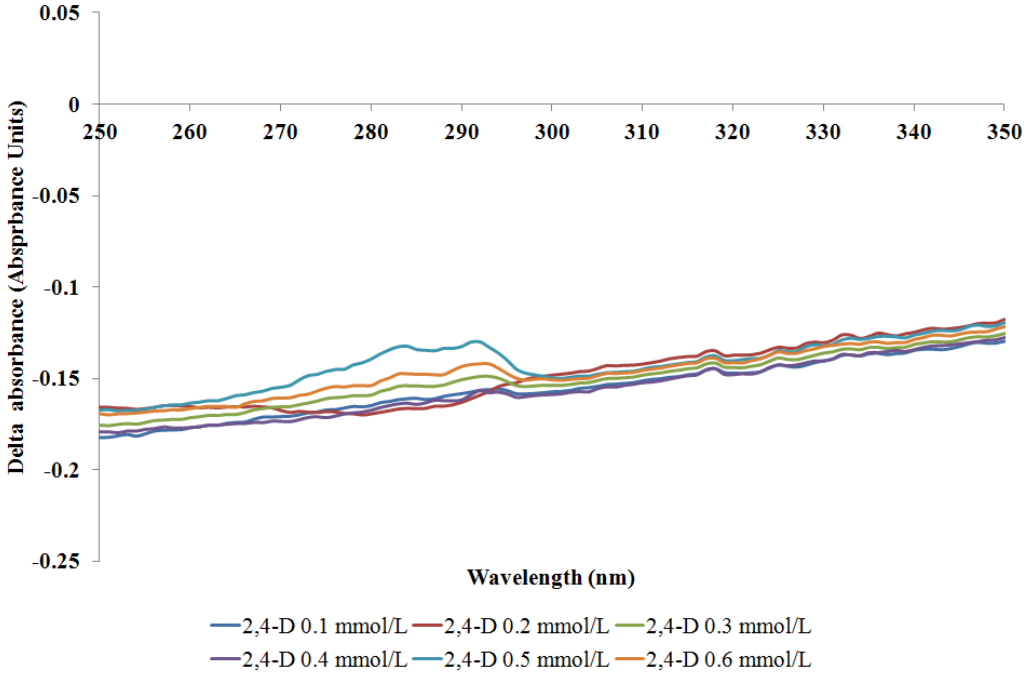


Figure 4.11: UV-Visible differential spectrum obtained from Figure 4.10 which contained 2,4-D (0.1 - 0.6 mmol/L) and HA (30 mg/L).

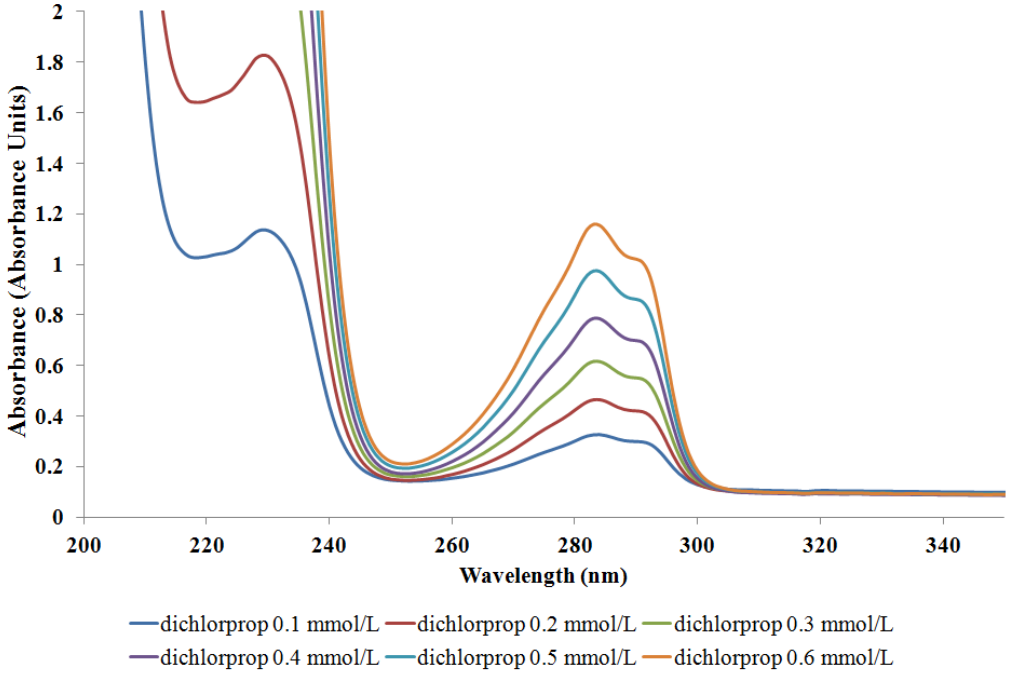


Figure 4.12: UV-Visible spectra for dichlorprop (0.1 - 0.6 mmol/L).

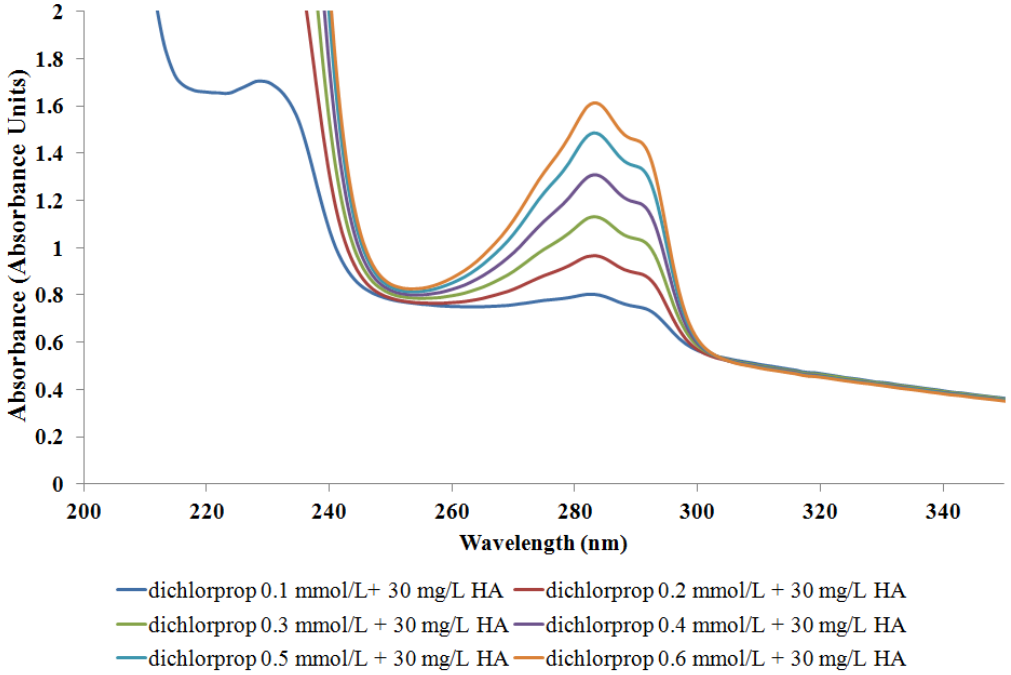


Figure 4.13: UV-Visible spectra for mixtures containing dichlorprop (0.1 - 0.6 mmol/L) and HA (30 mg/L).

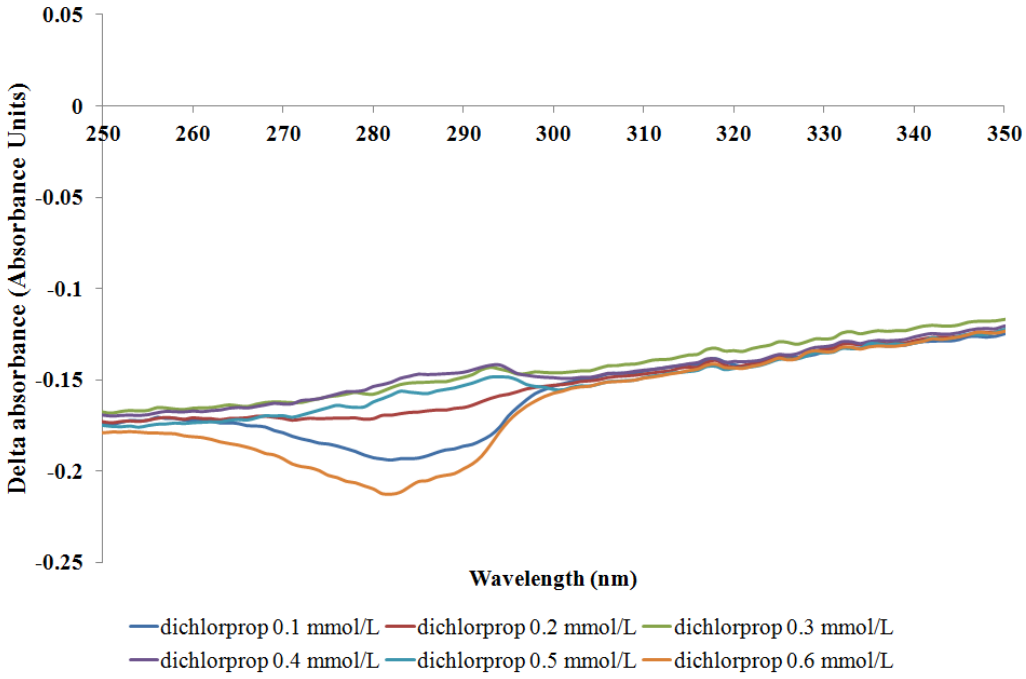


Figure 4.14: UV-Visible differential spectrum obtained from Figure 4.13 which contained dichlorprop (0.1 - 0.6 mmol/L) and HA (30 mg/L).

ever, as with dynamic quenching, the dependence of I^0 on the quencher is also linear. Static and dynamic quenching can be distinguished by measuring the lifetime of the fluorescence and differences in the absorption spectra. No change in absorption spectra is expected for dynamic quenching but changes can occur when a ground-state complex is formed. Fluorophores may be quenched by a combination of static (complex formation) and dynamic (collisions) quenching. In this case, the Stern-Volmer plot displays an upward curvature. The Perrin model describes static quenching between randomly distributed and immobile fluorophores which are accidentally in the proximity of the quencher [110, 111]. Therefore quenching only occurs when the quencher is inside a spherical volume. Therefore a linear slope of ln I^0/I vs. quencher concentration yields the quenching radius, R_s. Comparison of fluorescence intensity as a function of quencher concentration can therefore be used to assess whether the quenching is static, dynamic or a combination of both.

The fluorescence absorption spectra for humic acid sodium salt (Figure 4.16) was obtained by excitation at 330 nm and emission between 350 and 650 nm. Maximum fluorescence intensity was recorded at 460 nm. The HA spectrum obtained did not appear to be linear with respect to concentration. Initial increases in intensity were observed between 10 - 30 mg/L HA but a plateau was reached at higher concentrations. This may suggest a self quenching mechanism at higher concentrations.

Herbicide fluorescence data for MCPA, 2,4-D and dichlorprop (Figures 4.17 - 4.19) was obtained by excitation at 280 nm and observing the emission spectra between 285 and 370 nm. Maximum emission intensity was observed at 323 nm. Emission intensity for MCPA was concentration dependent and when the emission data vs. concentration from 0.01 - 0.09 mmol/L was plotted, a regression coefficient equal to 0.9918 was observed. However, a broader range from 0.1 - 0.6 mmol/L did not remain linear (R_2 = 0.6808) and plateaued from 0.4 - 0.6 mmol/L MCPA. Fluorescence data plotted for 2,4-D and dichlorprop was not linear and did not appear to be influenced by changes in herbicide concentration.

Comparison of the behaviour of the fluorescence intensity as a function of quencher concentration can yield insights into the nature of the interaction between the two compounds.

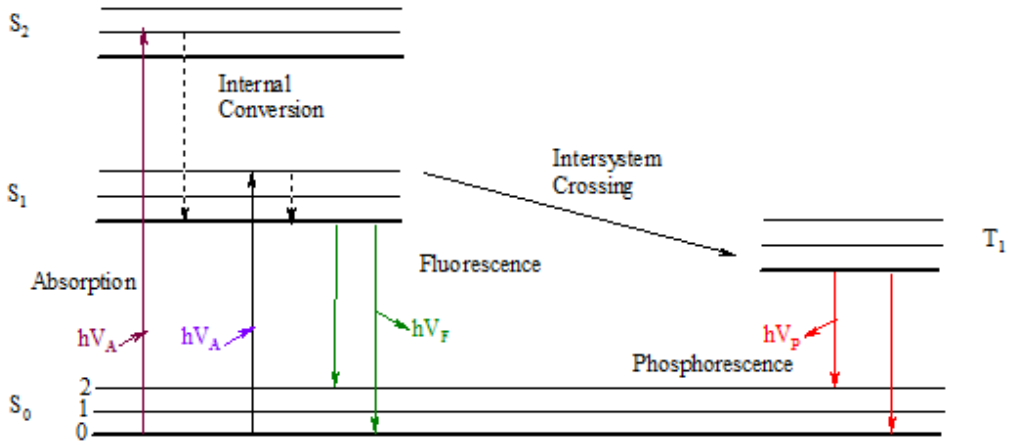


Figure 4.15: Jablonski diagram illustrating the molecular processes that can occur in the excited states when light is absorbed and emitted

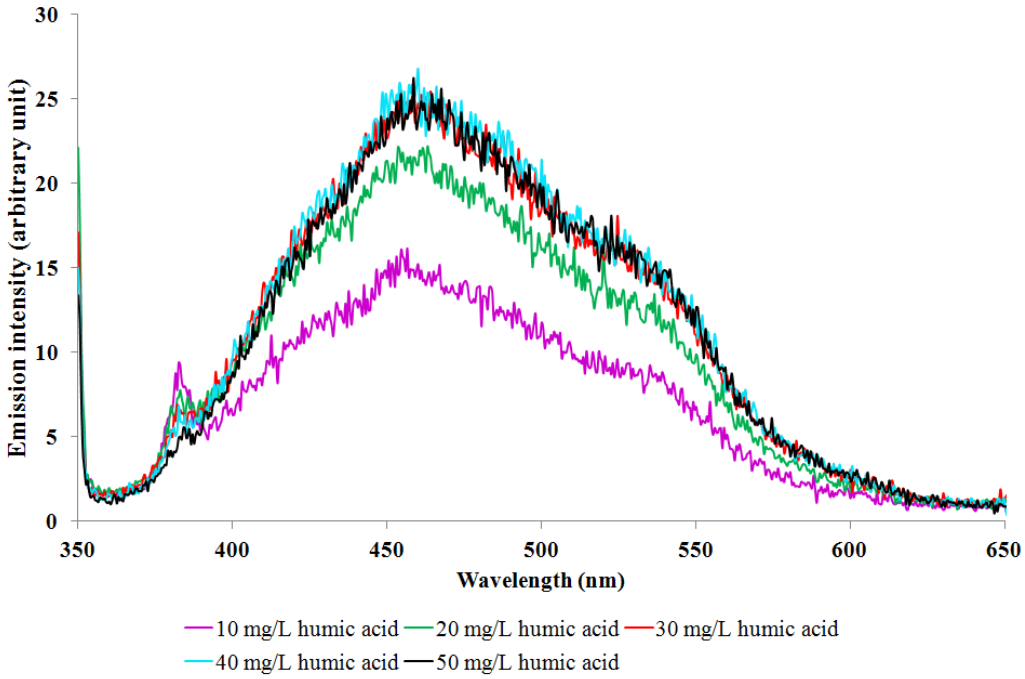


Figure 4.16: Fluorescence spectrum for humic acid sodium salt (10 - 50 mg/L).

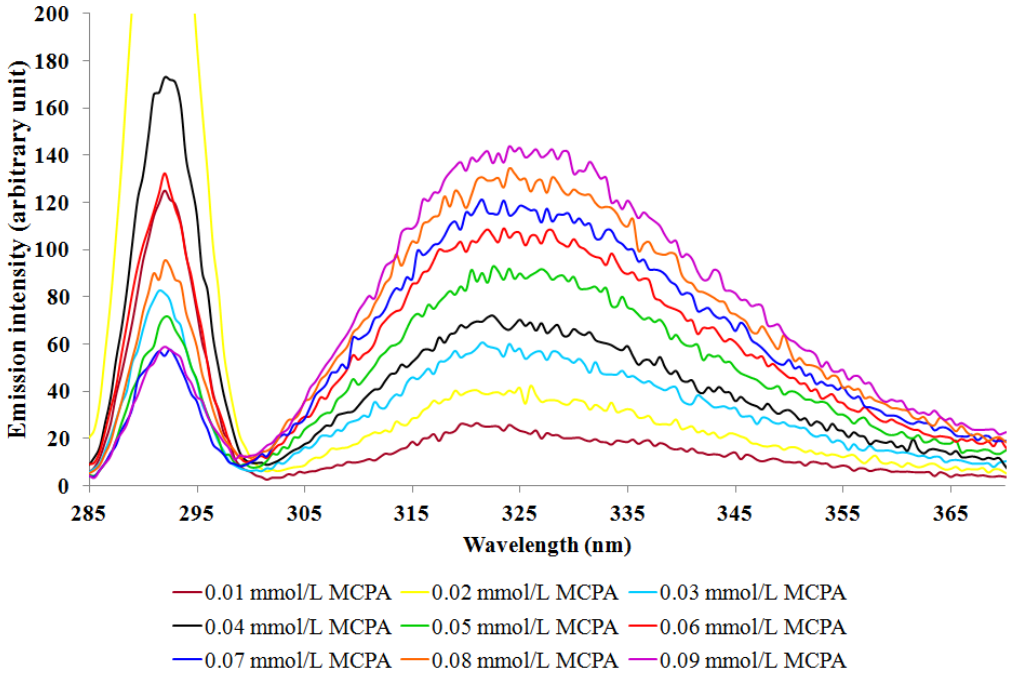


Figure 4.17: Fluorescence emission spectrum for 0.01 - 0.09 mmol/L MCPA.

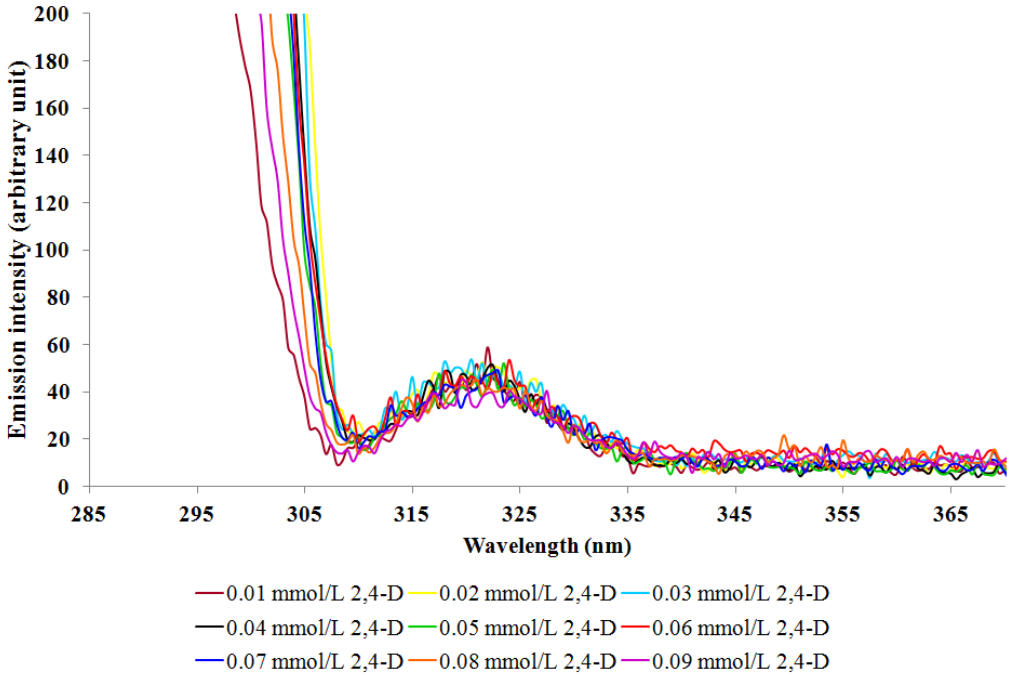


Figure 4.18: Fluorescence emission spectrum for 0.01 - 0.09 mmol/L 2,4-D.

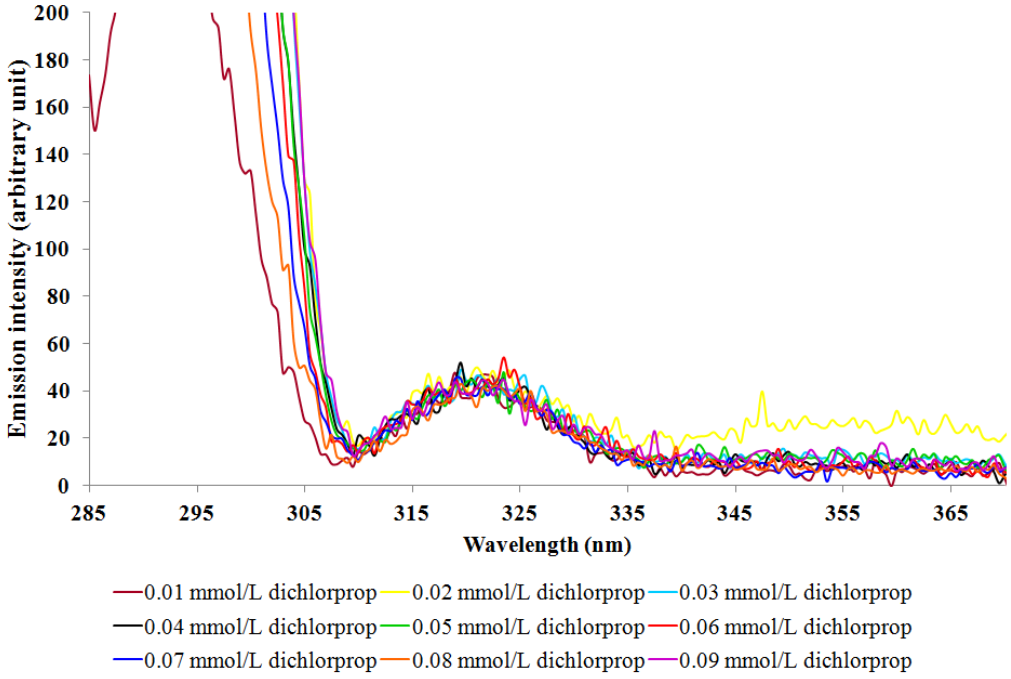


Figure 4.19: Fluorescence emission spectrum for 0.01 - 0.09 mmol/L dichlorprop.

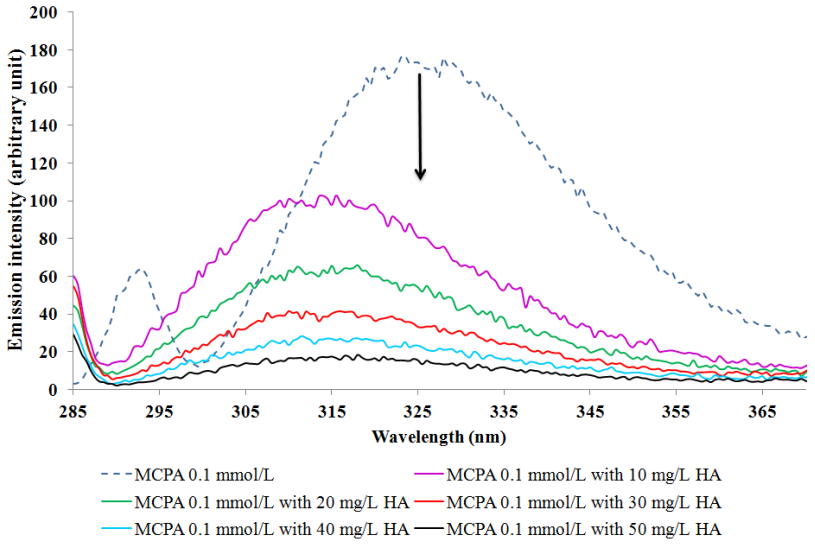


Figure 4.20: Fluorescence spectrum for MCPA fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

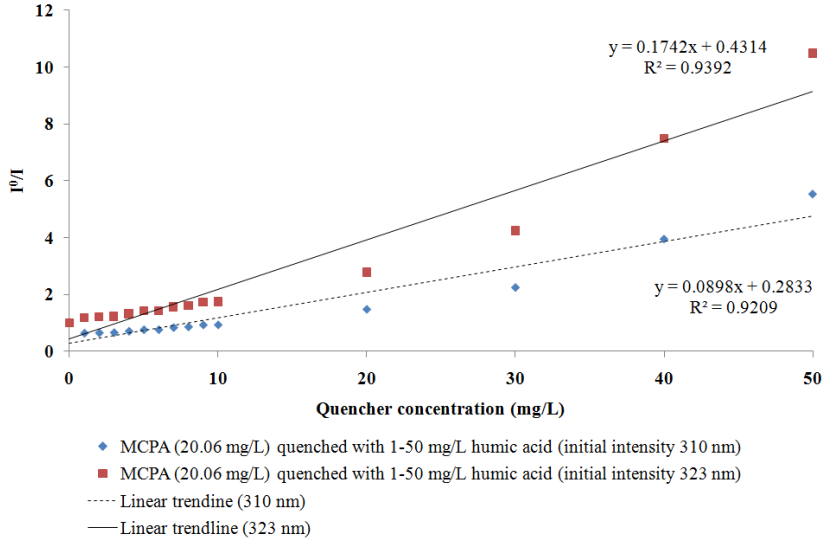


Figure 4.21: Stern-Volmer plot for MCPA fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

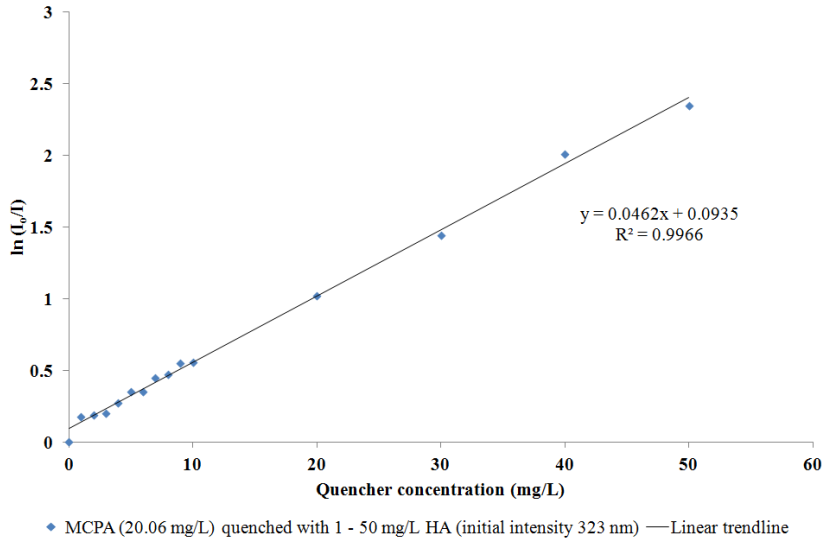


Figure 4.22: Perrin plot for MCPA fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

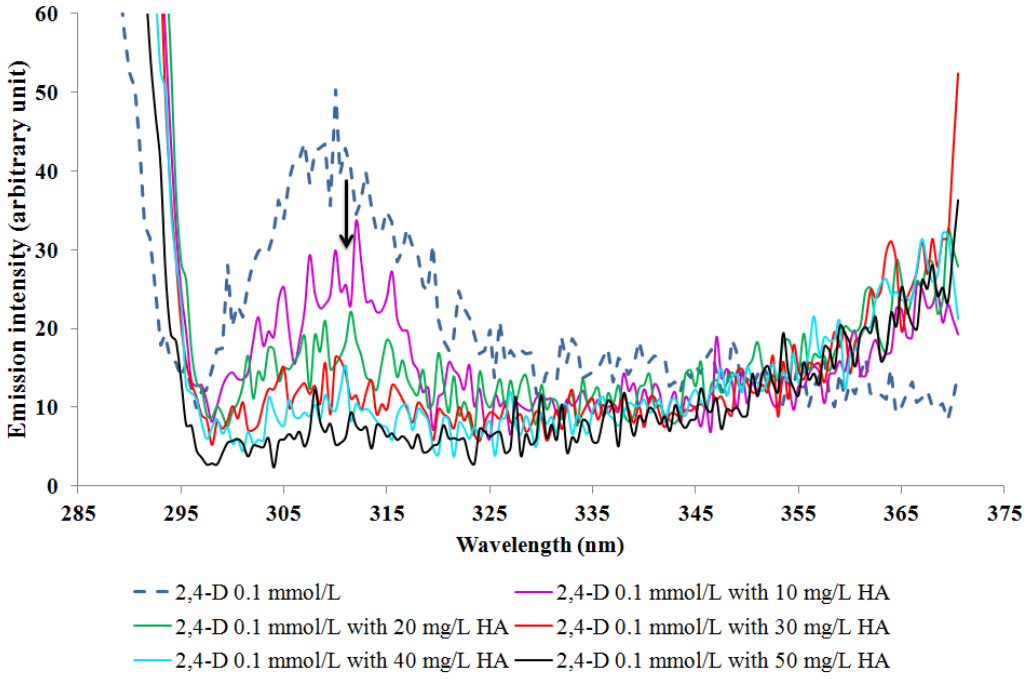


Figure 4.23: Fluorescence spectrum for 2,4-D fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

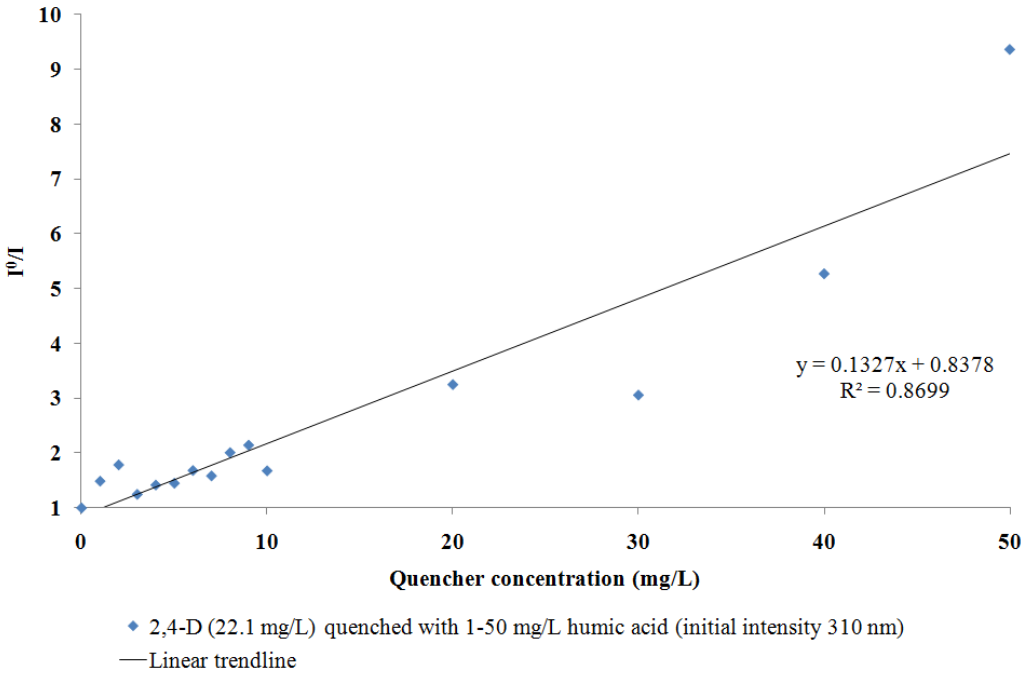


Figure 4.24: Stern-Volmer plot for 2,4-D fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

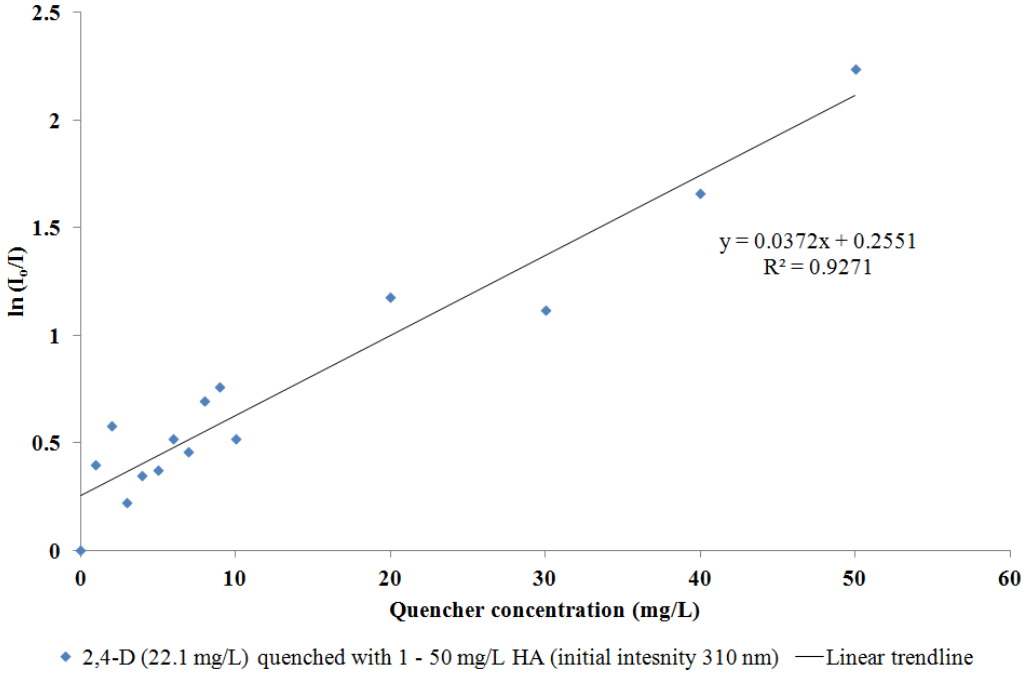


Figure 4.25: Perrin plot for 2,4-D fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

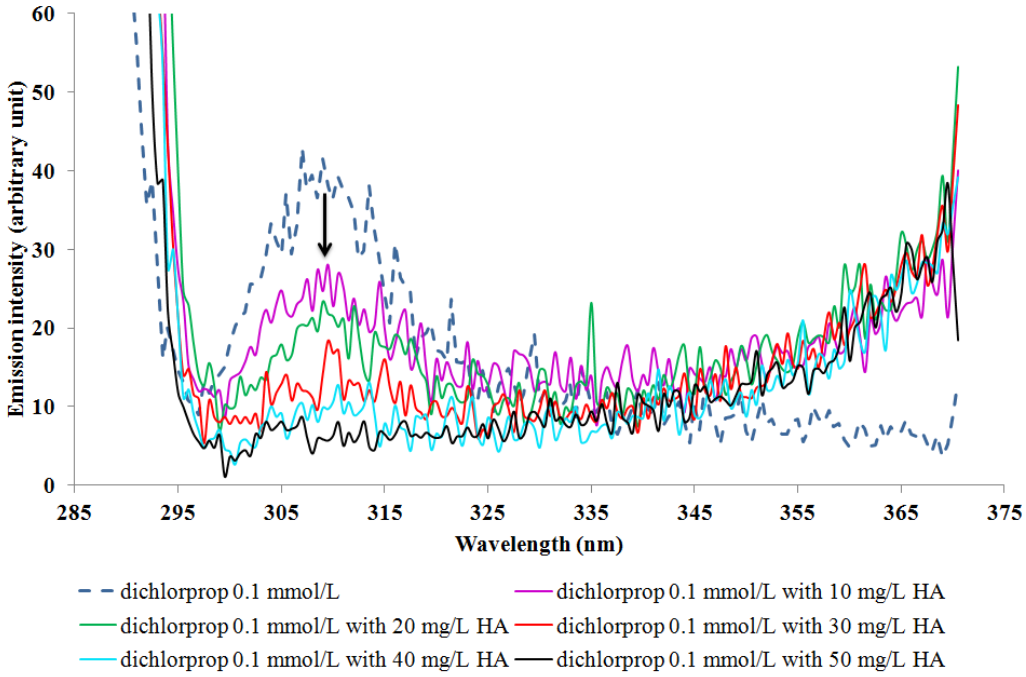


Figure 4.26: Fluorescence spectrum for dichlorprop fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

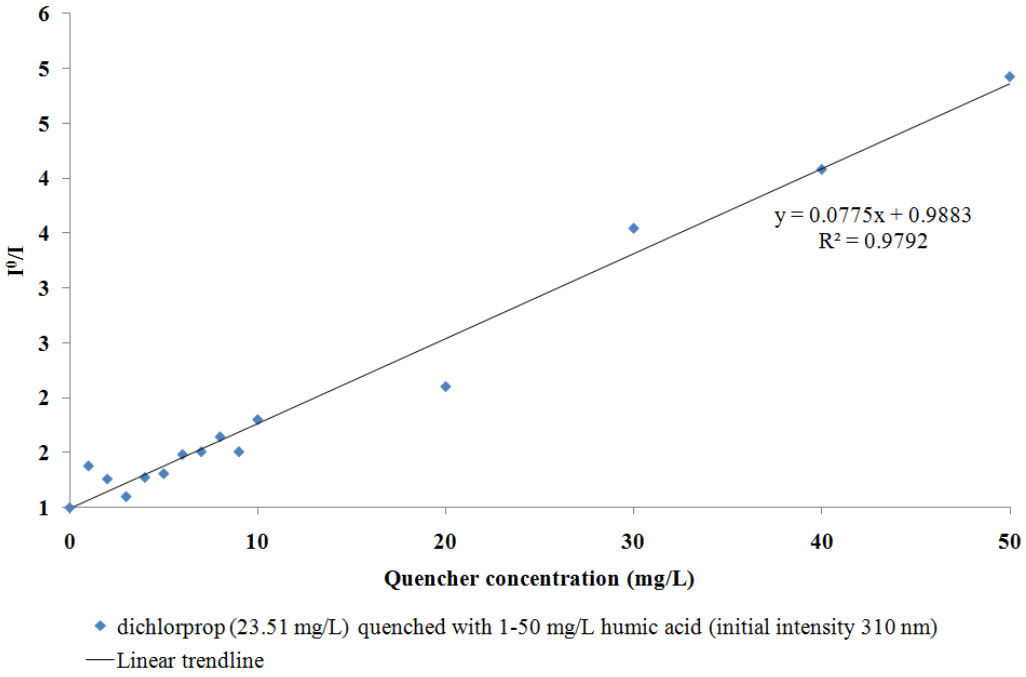


Figure 4.27: Stern-Volmer plot for dichlorprop fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

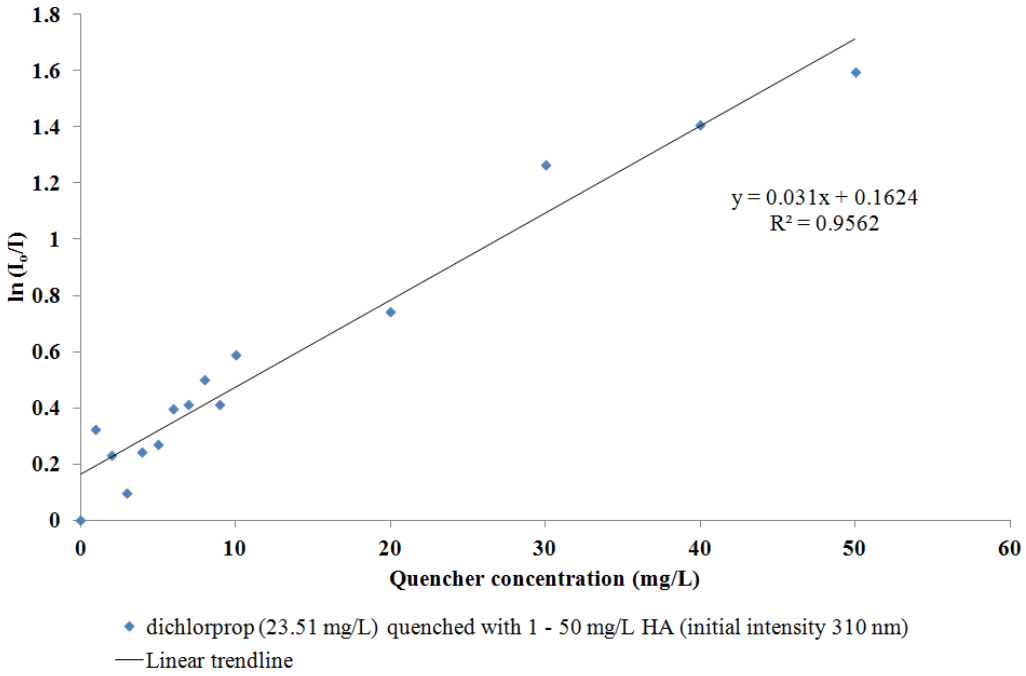


Figure 4.28: Perrin plot for dichlorprop fluorescence quenched with 10 - 50 mg/L humic acid sodium salt.

In this case it is the fluorescence intensity of MCPA, 2,4-D and dichlorprop (0.1 mmol/L) as a function of HA (1 - 50 mg/L) concentration. The herbicide emission intensity (I) was recorded at each HA concentration and compared to the herbicide intensity in the absence of the quencher (I^0). The Stern-Volmer and Perrin equations were then applied to the data. The MCPA fluorescence intensity centred at 310 nm decreased steadily upon addition of successive HA concentrations. However, the initial MCPA fluorescence λ_{max} without HA appeared at 323nm, and shifted to 310nm upon the addition of HA. As fluorescence is sensitive to any sample variations, it is possible that a change in pH (HA pH is ~ 8) may have caused this shift. Therefore both initial intensities at 310 and 323 nm were used to calculate the Stern-Volmer constant. When both values were applied, the shape of the Stern-Volmer plot remained constant but I^0/I values were higher for 323 nm. The MCPA Stern-Volmer plot depicted in Figure 4.21 follows an initial slope followed by an upward curvature. This plot would suggest a combination of static and dynamic quenching is occurring. The data obtained however, fits the Perrin model. The plot shown in Figure 4.22 shows a linear (R^2 0.9966) correlation to the Perrin equation. This data would suggest the presence of static quenching by proximity but the data for proximity could not to be calculated as the quencher concentration is in mg/L rather than moles. If the molecular weight of the humic acid was known, the quenching radius available to the humic acid could be calculated.

It has been reported that the spontaneous aggregation of aquatic solutions of humic substances can occur. Humic acids are natural polymers which in solutions are polydispersed as molecular and ionic fragments which can associate in different ways. Aggregations can occur at the intramolecular (single polymer molecule) or intermolecular (multiple chains) levels [112, 113]. At the intramolecular level, smaller constituents aggregate like surfactants [114], forming a spherical micelle with a non polar interior and a polar outer layer. Larger chains can fold and coil, forming intermolecular micelles. Hydrophobic solutes may be partitioned into the interior, isolated from the aqueous solution [115]. The fitting of the data to the Perrin model is due to quenching by proximity of the fluorophore to the quencher. The previous adsorption results have shown that some of the herbicide is unavailable for adsorption to the activated carbon. Based on the fluorescent results and the adsorption ex-

periments, it is possible that the herbicide may be surrounded by a humic acid micellular structure and therefore hindered from adsorbing to the activated carbon.

The fluorescence intensity data generated for both 2,4-D (Figure 4.23) and dichlorprop (Figure 4.26) was noisy when compared to the spectrum obtained for MCPA. Further analysis, changing the excitation wavelengths and slit width could further improve the fluorescence spectrum. The correlation to the Stern-Volmer plots and Perrin model (Figures 4.24 - 4.25 for 2,4-D and Figures 4.27 - 4.28 for dichlorprop) were similar to the fit observed for MCPA.

4.4 Conclusions and future work

The present work examined the adsorption of humic acid sodium salt to granular activated carbon and it's inhibiting effect on the uptake of chlorophenoxy herbicides. HA uptake by AC was minimal, possibly to the large molecular weight associated with HA. Herbicide adsorption to AC was hindered by the presence of HA in the sample solutions and by HA pre-saturated to the AC. Although pore blockage hindering herbicide access to the micropores has been used to describe the mechanism by which HA interferes with HA adsorption, lower adsorption was observed when the HA was in direct competition with the herbicides.

The possible interaction between herbicides and HA was investigated to evaluate any potential interactions occurring during site competition. The UV-Visible and fluorescence results represent initial experiments. Weak spectral changes were observed and the florescence intensity was quenched by HA addition, suggesting that some form of interaction occurs. However, with the current data it was not possible to distinguish what exactly is happening. Lifetime fluorescence experiments could distinguish between static and dynamic quenching. Additionally, a molecular weight has to be assigned to the humic acid used. The absence of this data makes extrapolating values from graphs difficult. The fit of the data to the Perrin model, suggests a form of quenching based on proximity of the fluorophore to the quencher. If the humic acid is forming a micelle around the herbicide, it is possible that this interaction is a) responsible for the quenching effect observed and b) a possible reason why the herbicide is not readily available for adsorption to AC when humic acid is present

in solution. Future work would include humic acid characterisation and fluorescent lifetime studies.

Chapter 5

Removal of chlorophenoxy herbicides from water: Using liquid core micro capsules as a comparison to activated carbon adsorption

5.1 Introduction

Liquid - liquid extraction (LLE) is one of the oldest analytical techniques available for pre-concentration and matrix isolation [116]. In addition to the time constraints and large solvent volumes [117] associated with LLE, the solvents could be harmful to the operator, expensive, and environmentally hazardous. Therefore simple LLE would not be a feasible method for drinking water treatment.

However, these restriction may be overcome by encapsulating the solvent within a hydrogel membrane. This encapsulation prevents contact between the two phases and the formation of emulsions. Liquid-core microcapsules are spherical particles less than 1 mm in diameter. The large inter-facial contact area enables a reduction in extraction rate. This novel methodology (termed capsular perstraction) of encapsulating a suitable hydrophobic solvent within a porous hydrogel membrane has previously been demonstrated [64, 66, 62, 63].

In this chapter, the feasibility of using liquid-core microcapsules as an alternative technique to activated carbon for the remediation of MCPA, 2,4-D and dichlorprop from water is investigated. Previously reported [64, 66] oil cores (dibutyl sebacate, miglyol 812 and oleic acid) were initially used. In addition a wider range of solvents including vegetable oils were screened as potential candidates for herbicide remediation and encapsulation.

5.2 Materials and methods

5.2.1 Chemicals

The herbicides were used as described in Section 2.2.1, page 52. HPLC grade methanol and formic acid (mass spectrometry grade) were purchased from Sigma Aldrich (Dublin, Ireland). Calcium chloride, 3-(N-Morpholino) propanesulfonic acid (MOPS), sodium chloride and Tween 80 were obtained from Fluka (Dublin, Ireland). Sodium alginate was purchased from Inotech Biotechnologies (Basel, Switzerland).

Herbicide solutions (0.5 mmol/L) were prepared in water using methanol as a co-solvent.

The herbicides were first dissolved in methanol before water was added. The final methanol concentration was 5 % (v/v). HPLC standards (0.1 - 0.6 mmol/L) were prepared by serial dilution from 10 mmol/L stock solutions prepared in methanol.

MOPS buffer was prepared with 10 mmol/L MOPS, 0.85 % (w/v) sodium chloride and adjusted to pH 7. Alginate stock solutions were prepared by dissolving alginate powder in MOPS buffer and mixing overnight on a magnetic stirrer. The alginate solution was vacuum filtered through a 0.22 μm PES (polyethersulfone) and a 0.22 μm PVDF (polyvinylidene fluoride)filter membrane (Millipore, Cork, Ireland) under a pressure of 2 bar. The gelling solution consisted of 32 g/L calcium chloride, 10 mmol/L MOPS (pH 7) and 0.2 % (v/v) Tween 80.

The solvents and oils used in liquid-liquid extractions and liquid cores are listed in Table 5.1. Activated Carbon, AquaSorb 2000 was manufactured by Jacobi Carbons and donated by Enva Ireland.

5.2.2 Experimental

5.2.3 Preparation of liquid core microcapsules

Liquid-core microcapsules (LCMs) were prepared by co-extrusion laminar jet breakup using an Inotech encapsuator (IE-50-R, Basel, Switzerland) fitted with an internal concentric nozzle of 200 μm and an external concentric nozzle of 300 μm. Spherical microcapsules were obtained by applying a set frequency to the jet containing alginate and organic phase protruding from the nozzle. The resulting vibration from the applied frequency broke up the jet into microcapsules, which landed in a magnetically stirred hardening bath. The hardening bath consisted of 32 g/L Cl_2, 10 mmol MOPS (pH 7) and 0.2 % (v/v) Tween 80 which was used to reduce surface tension. Octanol capsules could only be formed when the hardening bath was heated to 60 °C which further reduced the surface tension. Dibutyl sebacate capsules did not require this step. Coalescence was avoided by applying a negative electrostatic charge directly under the nozzle. LCMs recovered from the bath were analysed by microscopy to determine mean diameter size and standard deviation of the alginate outer

Table 5.1: Solvents and oils used in liquid-liquid extraction experiments.

Name	CAS	Density	Log K_{ow} ⋆	Supplier
Butyl Stearate	123-95-5	0.861 [a]	9.70	Sigma
Castor oil	8001-79-4	0.961 [b]	18.10	Sigma
Corn oil	8001-30-7	0.9 [b]	23.08	Sigma
Dibutyl sebacate	109-43-3	0.936 [b]	6.30	Aldrich
Dichloromethane	75-09-2	1.325 [b]	1.34	Riedel-de Haën
Dioctyl sebacate	122-62-3	0.94 [b]	10.08	Aldrich
Glycerol tributrate	60-01-5	1.032 [a]	3.31	Sigma
Isopropyl myristate	110-27-0	0.55 [b]	7.17	Sigma
Miglyol 812	73398-61-5◇	0.94 [b]	5.29	Sasol
Octanol	111-87-5	0.827 [b]	2.81	Riedel-de Haën
Oleic acid	112-80-1	0.89 [b]	7.73	Sigma
Oleyl alcohol	143-28-2	0.849 [b]	7.50	Sigma
Olive oil	8001-25-0	0.89 [b]	23.29	Sigma
Polypropylene Glycol 2000	25322-69-4	1.00 [b]	-0.21	Aldrich
Rapeseed oil	8002-13-9	0.91 [b]	7.09	Fluka
Soybean oil	8001-22-7	0.92 [b]	22.65	Sigma
Sunflower oil	8001-21-6	0.92 [b]	22.86	Aldrich

[a] g/mL at 20 °C
[b] g/mL at 25 °C
⋆ Log K_{ow} values were estimated using EPIWEB 4.1 KOWWIN Program (v1.68)
◇ Mixture containing decanoyl and octanoyl glycerides.

shell and the inner organic-core.

The schematic shown in Figure 5.1 from Inotech [118] shows the encapsulation process used for the production of LCMs with an Inotech encapsulator (Figure 5.2).

5.2.4 Measurement of capsule size distribution

The size and size distribution of the liquid core microcapsules was measured using a light microscope (model, BX-51, Olympus, Japan) attached to a camera (model DP30BW, Olympus, Japan) interfaced to a PC operating with Cell^F image analysis software (Olympus, Japan). One hundred microcapsules were measured individually using a magnification of x40 in order to determine the mean size and size distribution.

5.2.4.1 Liquid-liquid extraction

Aqueous samples containing 0.5 mmol/L herbicide in 100 mL volume and 5mL organic solvent were shaken overnight in a temperature controlled incubator shaker (Shel lab, SI series) at 100 RPM and 25 °C. The organic solvents used are listed in Table 5.1. Shake flask samples were prepared in triplicate including triplicate control samples containing only 0.5 mmol/L herbicide. Samples were taken from the shaker and left to settle for 2-3 hours. Aqueous phase samples were extracted by syringe and needle according to the OECD shake flask method [120] by blowing air through the needle while gently pushing it through the organic phase until the needle reached into the aqueous phase. The needle was removed and the sample transferred from the syringe to amber HPLC vials for analysis.

5.2.4.2 Capsular perstraction

Dibutyl sebacte (DBS) LCMs were recovered from the hardening bath and filtered through a porous mesh. Capsules weighing a total of 2.26 g (equal to 1.1 mL oil core) were incubated in water containing 0.5 mmol/L herbicide and agitated at 100 RPM at 25°C. A

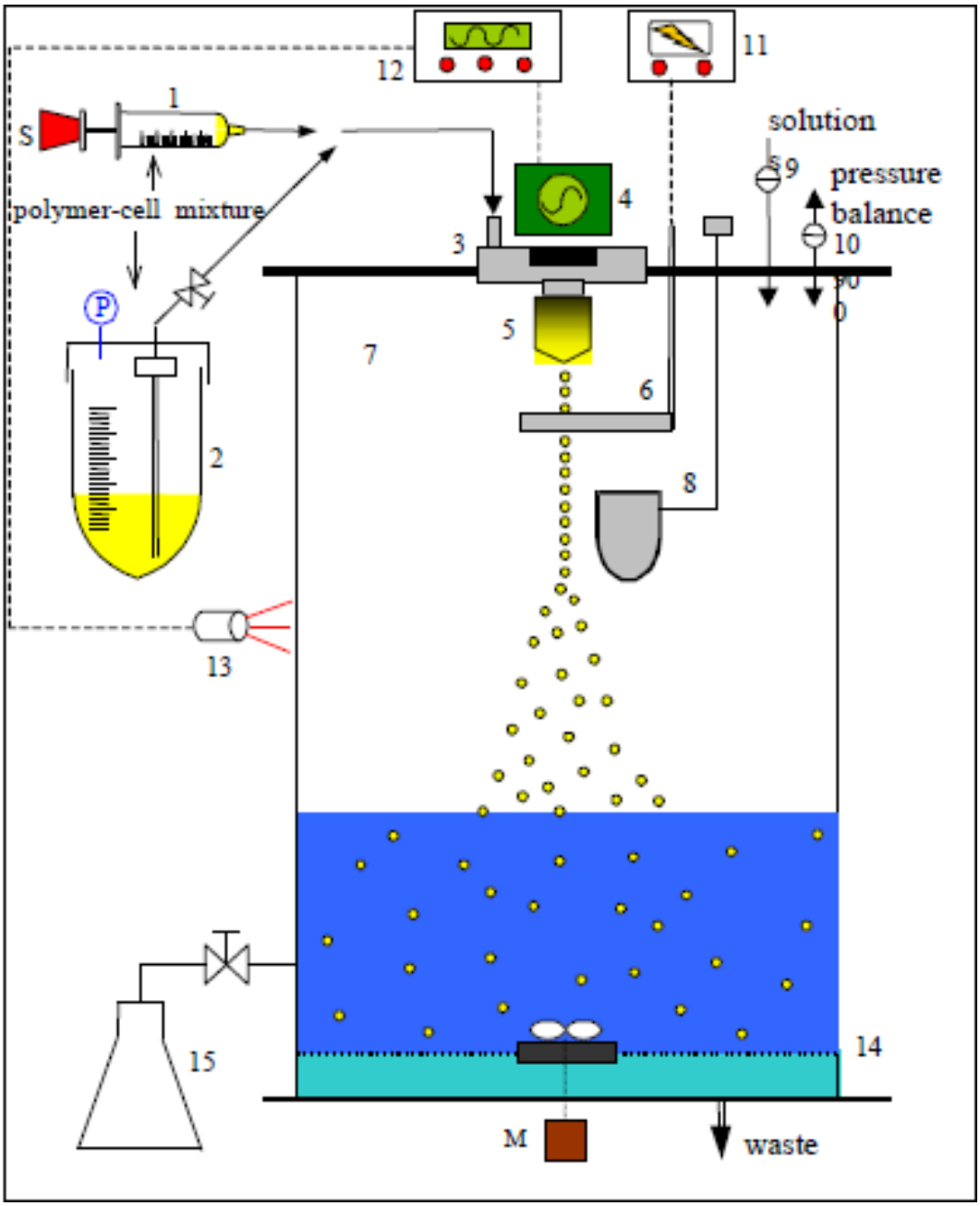


Figure 5.1: Schematic showing the LCM encapsulation process for an Inotech encapsulator. 1) Syringe 2) Pressure bottle 3) Pulsation chamber 4) Vibration system 5) Nozzle 6) Electrode 7) Reaction vessel 8) Bypass-cup 9) Liquid filter 10) Air filter 11) Electrostatic charge generator 12) Frequency generator 13) Stroboscope 14) Filtration grid 15) Bead collection flask M) Magnetic stirrer P) Pressure control system S) Syringe pump [118]

Figure 5.2: Inotech encapsulator (IE-50-R, Basel, Switzerland) [119]

constant volume of organic phase was achieved by measuring the capsule size (d_m) and the size of the liquid-core (d_lc). The total organic phase used was equal to 1 gram (1.1 mL) of dibutyl sebacate. Samples (0.2 mL) were extracted by syringe at 10 minute intervals over a 100 minute time period and analysed by HPLC. The experiment was replicated in triplicate including control samples containing no LCMs.

5.2.4.3 Herbicide removal by activated carbon adsorption

Aqueous 100 mL volume samples containing 0.5 mmol/L herbicide were contacted with 1 g AquaSorb 2000. Samples were prepared in triplicate including triplicate control samples containing no activated carbon. Samples were contained in 100 mL Duran flasks with lid shaken at 100 RPM at 25 °C. Samples (0.2 mL) were extracted by syringe at 10 minute intervals over a 100 minute time period and analysed by HPLC.

5.2.4.4 Activated carbon equilibrium studies

Aqueous 100 mL volume samples containing 0.5 mmol/L herbicide were contacted with 0.05 g AquaSorb 2000. Samples were prepared in triplicate including triplicate control samples containing no activated carbon. Samples were contained in 100 mL Duran flasks with lid and shaken overnight in a temperature controlled incubator shaker (Shel lab, SI series) at 100 RPM and 25 °C. These equilibrium samples were prepared for the purpose of comparing the results to liquid-liquid extraction experiments (Section 5.2.4.1).

5.2.5 Detection method

HPLC analysis was used as described in Section 2.2.2, page 53.

5.2.6 Determination of mass transfer

Mass transfer of the herbicides into the microcapsules were calculated using the following mass transfer equation:

$$V_{aq}(C^0_{aq} - C_{aq}) = V_m(C_m - C^0_m) \tag{5.1}$$

Where V_{aq} is the volume of the aqueous phase (bulk liquid) and is calculated by taking into account its dilution by water within the membrane of the microcapsule. C^0_{aq} and C_{aq} are the initial concentration and concentration at time t, respectively. V_m is the volume of the microcapsules. C^0_m and C_m are the herbicide concentrations within the microcapsule initially and at time t.

The partition coefficient, K is given as the concentration ratio between the herbicide in the microcapsule and the aqueous phase is calculated from;

$$K = \frac{C^e_m}{C^e_{aq}} \tag{5.2}$$

where C_m^e and C_{aq}^e are the herbicide concentration at equilibrium in the microcapsule and aqueous phase, respectively.

The volume of the capsule (sphere) and the liquid-core was calculated from:

$$Volume = \frac{4}{3}\pi r^3 \tag{5.3}$$

5.3 Results and discussion

5.3.1 Solvent selection

The solvents chosen for potential encapsulation have previously been used to extract a variety of pesticides [66] , pharmaceuticals [64] and other hydrophobic compounds [62, 63] from aqueous solutions. Dibutyl sebacate, miglyol 812 and oleic acid liquid-liquid shake flask extraction experiments for MCPA, 2,4-D and diclorprop were performed as described in Section 5.2.4.1. The concentration of herbicide extracted are shown in Figure 5.3. The results were calculated from the experimental data, representing the herbicide extraction in mmol/L by 1g of oil. Based on the higher affinity for the selected herbicides, dibutyl sebacate was chosen as the oil core.

5.3.1.1 Capsular perstraction of herbicides using dibutyl sebacate liquid-core microcapsules

Dibutyl sebacate (DBS) capsules (Figure 5.4) with a d_m of 387.45 μm $\pm$ 3.65 % and a d_lc of 273.64μm $\pm$ 2.95 % were produced and retained according to the method described in Section 5.2.3. The number of microcapsules used was equal 1 g of oil contained within the capsules. From Figure 5.5 it can be seen that MCPA, 2,4-D and dichlorprop are extracted from the aqueous phase. Equilibrium is reached after 60 minutes with 15 %, 9 % and

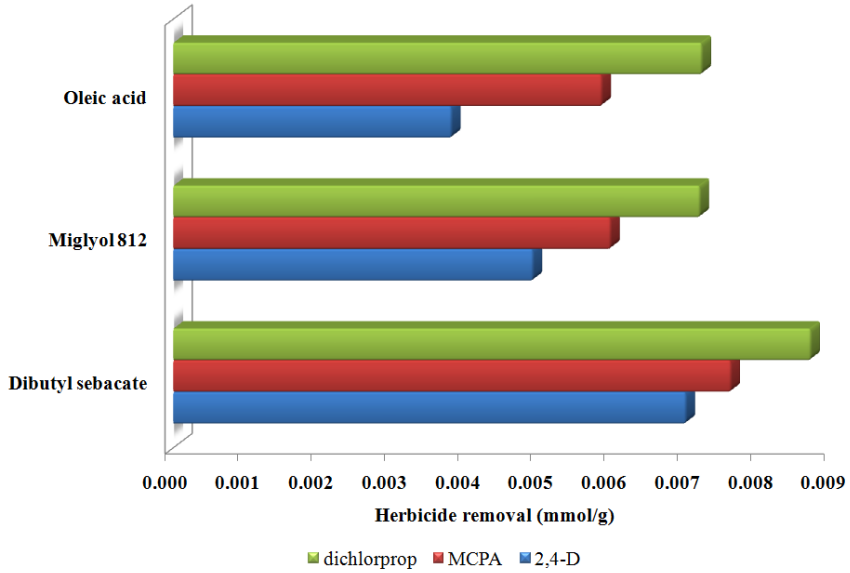


Figure 5.3: MCPA, 2,4-D and dichlorprop (0.5 mmol/L) liquid-liquid extraction from water using dibutyl sebacate, miglyol 812 and oleic acid. Results represent herbicide removal per gram of oil (calculated from experimental values obtained and density.)

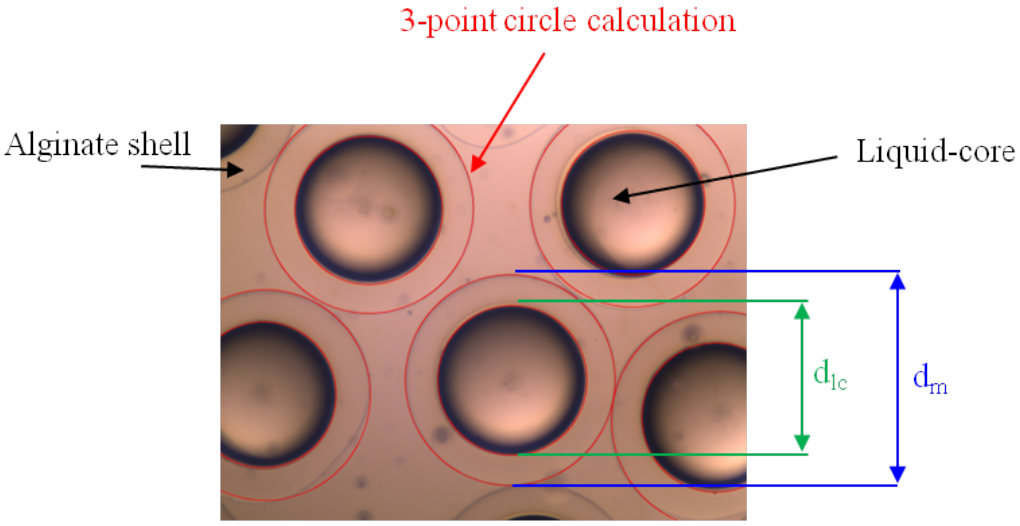


Figure 5.4: Light microscope image of dibutyl sebacate liquid-core microcapsules used to extract MCPA, 2,4-D and dichlorprop from water. Capsules displayed have a d_m of 387.45 μm $\pm$ 3.65 % and a d_lc of 273.64 μm $\pm$ 2.95 %.

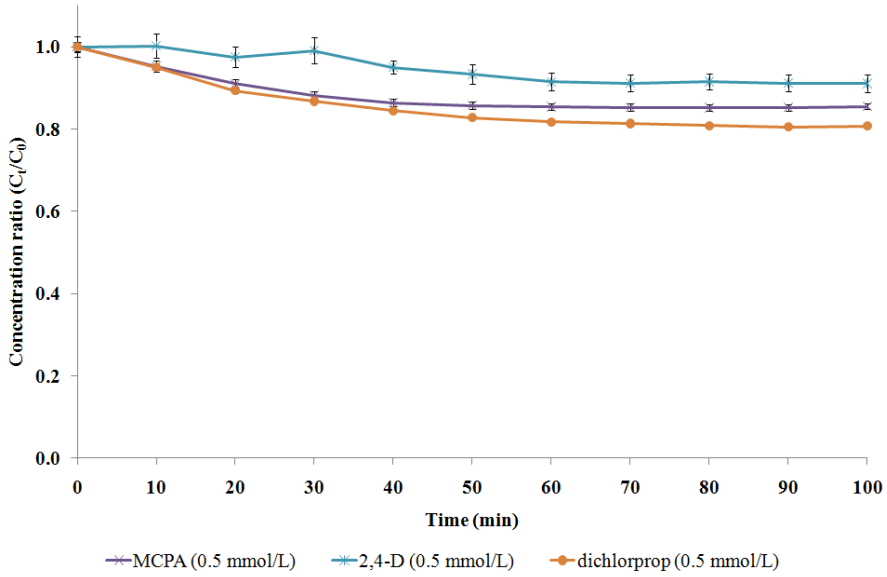


Figure 5.5: Capsular perstraction for MCPA, 2,4-D and dichlorprop (0.5 mmol/L) from water using dibutyl sebacate liquid-core microcapsules. C_t/C_0 represents a ratio of the concentration at time t to the initial concentration.

18 % MCPA, 2,4-D and dichlorprop extracted, respectively. Higher levels of extraction could be achieved by increasing the number of microcapsules used. The quantity (1 g of oil) used here was selected as a standard metric value to be compared to activated carbon experiments.

5.3.1.2 Liquid-core microcapsule perstraction compared to activated carbon adsorption

The comparison between liquid-core microcapsule perstraction and activated carbon adsorption is difficult. Activated carbon (AC) possess a large surface area and a complex surface chemistry where organic and non polar adsorbates are retained in an equilibrium process. AC can be manufactured according to the application but may not be very selective. Microcapsules consist of a liquid organic core surrounded by a hydrophilic membrane, attracting pollutants across the membrane and capturing it in the liquid core. These capsules have an enormous surface area to volume ratio, allowing rapid organic pollutant removal. The microcapsules can be designed to increase selectivity for specific compounds.This dif-

Table 5.2: AquaSorb 2000 adsorption capacity for herbicides and the calculated estimate from experimental values detailing how much activated carbon is required to remove 0.5 mmol/L herbicide from aqueous solution under experimental conditions.

Herbicide	adsorption capacity (mmol/g)	g required to remove 0.5 mmol/L
MCPA	0.4194	1.19
2,4-D	0.4044	1.24
dichlorprop	0.3887	1.29

Table 5.3: DBS oil liquid-liquid extraction for herbicides and the calculated estimate from experimental values detailing how much DBS oil is required to remove 0.5 mmol/L herbicide from aqueous solution under experimental conditions.

Herbicide	extraction per gram of oil (mmol/g)	g required to remove 0.5 mmol/L
MCPA	0.0076	65.79
2,4-D	0.0070	71.43
dichlorprop	0.0087	57.47

ference in material structure, selectivity and mode of action is difficult to compare and hence a standard weight unit was chosen as a comparison.

Figure 5.6 shows the extraction and adsorption behaviour for MCPA, 2,4-D and dichlorprop when treated with 1 g DBS LCMs and 1 g AquaSorb 2000 over 100 minutes. As shown previously, LCMs reach equilibrium after 60 minutes. However, AC adsorption had not reached equilibrium after 100 minutes. The remediation by AC adsorption had removed an average of 70 % of each herbicide after 100 minutes compared to 14 % by LCM perstraction. The experimental results obtained from liquid-liquid extraction and AC equilibrium studies were used to calculate approximately how many grams of DBS oil and AquaSorb 2000 would be required to remove 0.5 mmol/L MCPA, 2,4-D or dichlorprop from aqueous solutions. The results are listed in Table 5.2 and Table 5.3. For example, the removal of 0.5 mmol/L MCPA by DBS oil would require a 55 fold increase in the gram quantity needed for remediation compared to the use of activated carbon.

5.3.2 Solvent screening

Maximum herbicide extraction per gram of solvent (Figure 5.7) was calculated from liquid-liquid extraction results. Differences in extraction results were observed depending on sol-

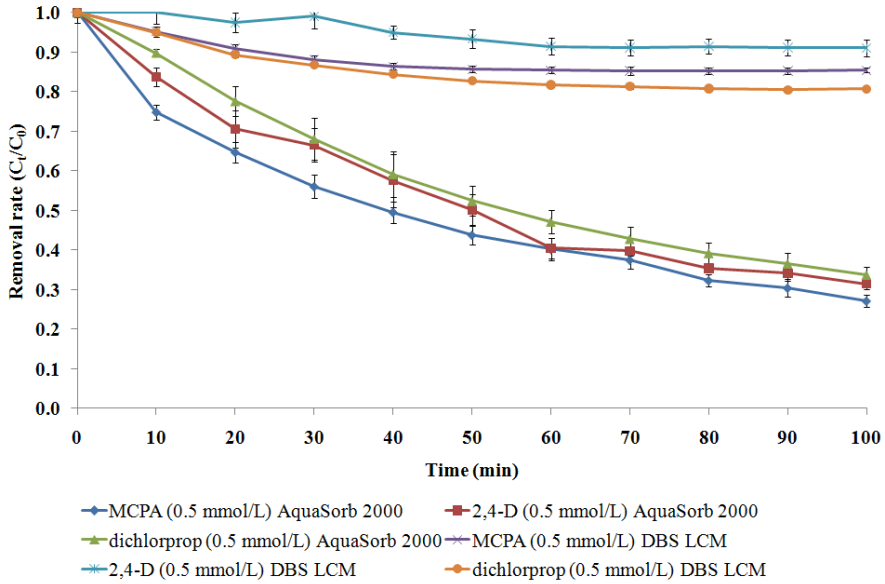


Figure 5.6: Removal rates for MCPA, 2,4-D and dichlorprop (0.5 mmol/L) from water using dibutyl sebacate liquid-core microcapsules and activated carbon. C_t/C_0 represents a ratio of the concentration at time t to the initial concentration.

vent choice and herbicide used. Maximum extraction followed the order of dichlorprop $>$ MCPA $>$ 2,4-D for all solvents. This result complies with previous kinetic experiment with dibutyl sebacate microcapsules and may be attributed to differences between the hydrophobic properties of each herbicide. Functional group comparison between oleyl alcohol and oleic acid suggested a more favourable extraction by the alcohol group compared to the acid group. Similarly, a decrease in extraction was observed when the chain length was increased from dibutyl sebacate to dioctyl sebacate. Maximum herbicide extraction by octanol suggests a microcapsule containing this oil would be more effective than the previously tested dibutyl sebacate core.

5.3.3 Octanol liquid core microcapsules

The production of a new LCMs (Figure 5.8) containing an octanol core surrounded by an alginate outer shell was successful. Initially the microcapsules were produced by the same method described in Section 5.2.3 for DBS LCMs. However, the surface tension of the hardening bath was too high and the capsules burst on impact, resulting in the formation of

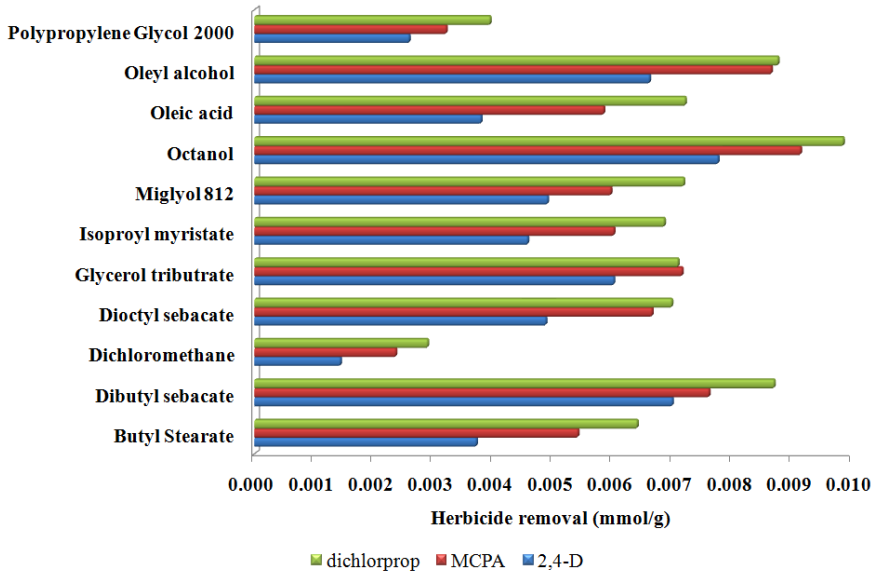


Figure 5.7: MCPA, 2,4-D and dichlorprop (0.5 mmol/L) liquid-liquid extraction from water. Results represent herbicide removal per gram of oil (calculated from experimental values obtained and density).

Table 5.4: Octanol liquid-liquid extraction for herbicides and the calculated estimate from experimental values detailing how much octanol is required to remove 0.5 mmol/L herbicide from aqueous solution under experimental conditions.

Herbicide	extraction per gram of oil (mmol/g)	g required to remove 0.5 mmol/L
MCPA	0.0091	54.95
2,4-D	0.0078	64.10
dichlorprop	0.0099	50.51

empty alginate shells. The surface tension was reduced by heating the hardening bath from room temperature to 60 °C. The reduction in surface tension prevented further bursting and enabled the formation of octanol LCMs.

Although the production of these capsules was successful, subsequent instrument failures and time restraints towards the end of the allocated project time prevented further experiments to be completed. However, the experimental data obtained from liquid-liquid extraction experiments was analysed and compared to the activated carbon results (Table 5.2). This data, shown in Table 5.4 shows that approximately 55, 64 and 51 grams of octanol would be required to remove 0.5 mmol/L MCPA, 2,4-D and dichlorprop, respectively.

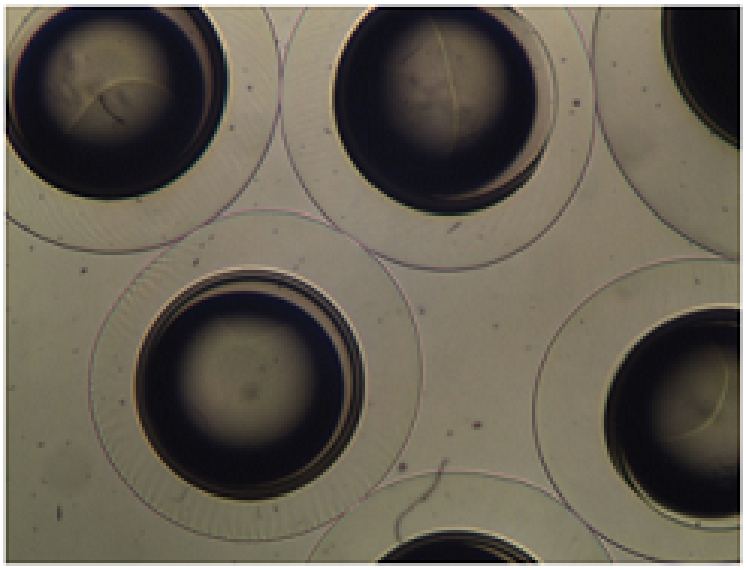


Figure 5.8: Light microscope image of octanol liquid-core microcapsules.

5.3.4 Castor oil liquid core microcapsules

The Drinking Water Inspectorate (DWI) provides independent reassurance that water supplies in England and Wales are safe and of acceptable quality for human consumption. The DWI has listed sodium alginate ($<$ 0.5 mg/L) as an approved chemical in drinking water treatments for the removal of colloidal and fie suspended particles [121]. However, the core materials used may need to undergo separate evaluation and approval before implementation in drinking water treatment plants or approved pilot plant studies could commence [122]. Although the liquid core inside the alginate shell is stable and fully encapsulated, a more environmentally friendly and cheaper core material could be desirable. The selection of vegetable oils was thus proposed. The large scale production of vegetable oils for the bio-diesel industry [123, 124, 125] and their availability as a natural and biodegradable product could potentially be a more environmentally friendly option to organic solvents.

This study focused on castor, corn, rapeseed, sunflower, soybean and olive oil. Partition coefficient and herbicide removal results (Figure 5.9) showed a higher level of activity for castor oil compared to the other oils tested. Castor oil was 20 % less effective than octanol at extracting the herbicides from water. Corn, rapeseed, sunflower, soybean and olive oil extraction results were similar, suggesting that the composition of castor oil or possibly Log

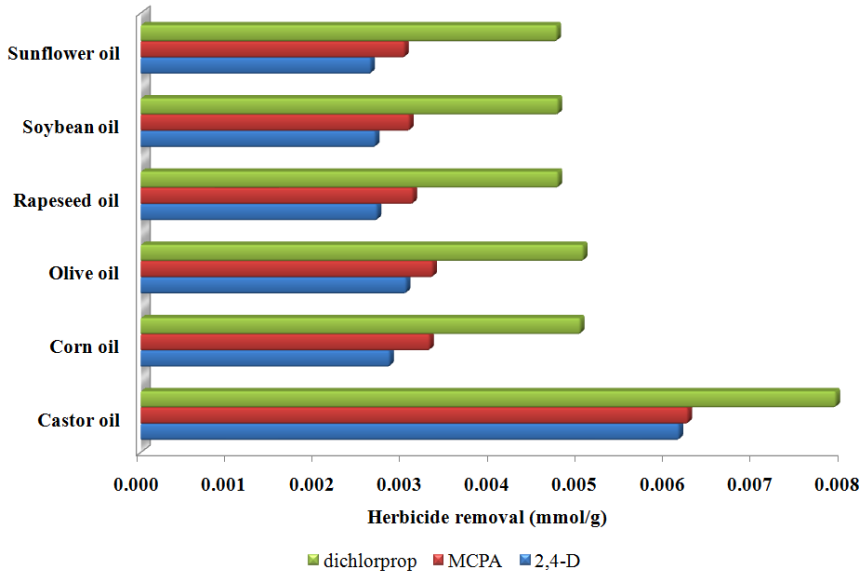


Figure 5.9: MCPA, 2,4-D and dichlorprop (0.5 mmol/L) liquid-liquid extraction from water using vegetable oils. Results represent herbicide removal per gram of oil (calculated from experimental values obtained and density).

K_{ow} values were the attributing factor. The Log K_{ow} values for each oil are listed in Table 5.1.The Log K_{ow} values for Corn, olive, soybean and sunflower oil are similar between 22 and 23. Castor oil Log K_{ow} is lower (18.10), while rapeseed oil had the lowest Log K_{ow} value (7.09). However, in this case the oil with the lowest Log K_{ow} value is not the most efficient at extracting MCPA, 2,4-D and dichlorprop. Castor oil is composed of 90 % ricinoleic acid and is the only vegetable oil with such a high content of fatty hydroxyacids [126]. The remaining 20 % comprises of oleic acid, linoleic acid, stearic acid and palmitic acid. Sunflower [127], corn [128], rapeseed [129], soybean [130] and olive oil are mainly comprised of linoleic, oleic,stearic and palmitic acids and contain no ricinoleic acid.

The production of castor oil LCMs however, was unsuccessful due to the high viscosity of castor oil. It may be possible to encapsulate castor oil if the viscosity could be reduced, for example using a heated nozzle system attached to the encapsulator. However, the experimental data obtained from liquid-liquid extraction experiments was analysed and compared to the activated carbon results (Table 5.2). This data, shown in Table 5.5 shows that approximately 81, 82 and 63 grams of octanol would be required to remove 0.5 mmol/L MCPA, 2,4-D and dichlorprop, respectively.

Table 5.5: Castor oil liquid-liquid extraction for herbicides and the calculated estimate from experimental values detailing how much castor oil is required to remove 0.5 mmol/L herbicide from aqueous solution under experimental conditions.

Herbicide	extraction per gram of oil (mmol/g)	g required to remove 0.5 mmol/L
MCPA	0.0062	80.65
2,4-D	0.0061	81.97
dichlorprop	0.0079	63.29

5.4 Conclusions and future work

Capsular perstraction of MCPA, 2,4-D and dichlorprop by dibutyl sebacate liquid-core microcapsules was demonstrated. The use of LCMs results in between 9 and 18 % of the herbicides being extracted within 60 minutes of capsule addition. The quantity of LCMs added was equal to 1 g of oil core and could be increased to achieve higher levels of extraction. The results were compared to adsorption by 1 g of activated carbon (AquaSorb 200) over the same time period of 100 minutes. Additional solvents were screened as potential liquid-cores with a higher affinity for the herbicides than dibutyl sebacate.Based on these results, octanol was selected as a new core material for encapsulation. The production of octanol LCMs was initially unsuccessful when the production method used for DBS LCMs was applied. The capsules burst on impact with the hardening solution. The surface tension was reduced by heating the hardening bath to 60 °C and this facilitated the production of spherical octanol LCMs. A comparison of DBS and octanol capsules was not completed but would be feasible for future work.

Vegetable oils were screened as possible candidates for non-toxic environmentally friendly oil cores. Castor oil was the most efficient vegetable oil for herbicide extraction. Unlike the other oils tested, castor oil contains 90 % ricinoliec acid and this may be the active ingredient responsible for the higher efficiency compared to major components such as oleic and linoleic acid present in other vegetable oils. Castor oil capsules were not successfully obtained due to production limitations with a high viscosity oil. It may be possible to produce and test castor oil capsules by modifying the encapsulator instrument with a heated nozzle system, therefore reducing the viscosity of the oil.

Although the initial herbicide values used here do not reflect concentrations typically found in drinking water, the experiments using liquid core microcapsules demonstrate their ability to capture and retain the selected herbicides. Commercialisation and pilot plant studies using LCMs could be undertaken in the future to estimate their commercial potential in the drinking water treatment process. However, alternative applications such as on-site spill response in industries where herbicides are used in large quantities or treatment of water used to clean contaminated herbicide spraying/application equipment could be feasible.

Chapter 6

Final discussion, conclusions and future work

6.1 HPLC method

The development of a rapid HPLC method, which unlike GCMS methods did not require further derivatization of the herbicide samples, was key to develop the quantitative analysis technique required in this study. By eliminating the need to derivatize the chlorinated herbicides, less toxic solvents were required and time was saved. The method was validated, giving certainty that the method would produce reliable and accurate results. A gradient method for multiple sample analysis was initially developed. However, only partial separation was achieved, therefore further and complete separation of two compounds differing by a chlorine group would be difficult to achieve and validate. Extensive method development involving changes in flow rates, solvent composition and varying the formic acid content could produce a valid gradient method used to separate chlorophenoxy herbicides.

6.2 Removal of chlorophenoxy herbicides by activated carbon adsorption

Both powdered and granular activated carbons were used in this study, of which two granular types (AquaSorb 2000 and Norit 1240W) are currently implemented in drinking water treatment plants. Unlike granular ACs, the powdered type (BP2 ColorSorb) is not implemented in fixed bed filters, but is added in a dosing step and is later removed by filtration. A third granular AC type (Sigma Aldrich C-3014) was tested in the form of an untreated standard laboratory grade carbon. In the case of each activated carbon, the adsorption process was controlled by the dissociation of MCPA, 2,4-D and dichlorprop and the surface chemistry of the activated carbons. The adsorption capacity of the activated carbons was decreased as pH increased. Adsorption intensity parameters for both the Langmuir and Freundlich isotherm models showed that the adsorption was a favourable process for each herbicide on all four activated carbons investigated.

6.3 The interaction between humic acid, activated carbon and chlorophenoxy herbicides

The activated carbon adsorption system was altered by the addition of humic acid sodium salt. It was predicted that when humic acid was adsorbed it would inhibit the uptake of herbicides by blocking access to the micro-porous structure of the carbon. However, the uptake of humic acid by AC adsorption was minimal and when the AC was recovered and reused, the adsorption capacity was slightly decreased. Direct addition of humic acid into the solution containing herbicide and activated carbon showed the biggest decrease in herbicide uptake. Further investigation into the interaction between the humic acid and herbicides showed that fluorescence data fitted the Perrin model, suggested a possible humic acid micellular structure forming around the herbicide. If the humic acid is forming a micelle around the herbicide, it is possible that this interaction is a) responsible for the quenching effect observed and b) a possible reason why the herbicide is not readily available for adsorption to AC when humic acid is present in solution. Future work would include humic acid characterisation to determine the molecular weight and elemental composition. If the molecular weight of the humic acid was known, the quenching radius available to the humic acid could be calculated. Fluorescence lifetime studies could be a valuable addition to this study. The results would clarify if the quenching observed is static or dynamic.

6.4 Chlorophenoxy herbicide remediation by liquid-core microcapsule perstraction

A novel perstraction system using liquid-core microcapsules was used as a comparison to activated carbon adsorption. LCMs containing dibutyl sebacate successfully removed MCPA, 2,4-D and dichlorprop from aqueous solutions. However, when compared to activated carbon, this method was less effective. An alternative octanol core was suggested after promising liquid-liquid extraction results. Octanol capsules were successfully encapsulated within an alginate membrane. Castor oil was investigated as an environmentally

friendly alternative to solvents but was difficult to encapsulate due to its high viscosity. It is suspected that the ricinoleic acid (90 %) content in castor oil has a high affinity for the chlorophenoxy herbicides. Future work with the LCMs would begin by testing the performance of octanol LCMs against dibutyl sebacate LCMs. This would be followed by a study into parameters which enhance the perstraction process. Examples of these parameters would include pH, RPM, ionic strength and temperature. Additionally, recovery of the herbicides trapped within the core and the recycling of the capsules could be considered.

6.5 Comparing activated carbon adsorption to liquid-core microcapsule perstraction

The removal of MCPA, 2,4-D and dichlorprop, a group of chlorophenoxy herbicides, was achieved by both activated carbon adsorption and liquid-core microcapsule perstraction. The comparison between liquid-core microcapsule perstraction and activated carbon adsorption is difficult. Activated carbon (AC) possess a large surface area and a complex surface chemistry where organic and non polar adsorbates are retained in an equilibrium process. AC can be manufactured according to the application but may not be very selective. Microcapsules consist of a liquid organic core surrounded by a hydrophilic membrane, attracting pollutants across the membrane and capturing it in the liquid core. These capsules have an enormous surface area to volume ratio, allowing rapid organic pollutant removal. The microcapsules can be designed to increase selectivity for specific compounds.This difference in material structure, selectivity and mode of action is difficult to compare and hence a standard weight unit was chosen as a comparison. The extraction and adsorption behaviour for MCPA, 2,4-D and dichlorprop when treated with 1 g DBS LCMs and 1 g AquaSorb 2000 over 100 minutes showed that LCMs reach equilibrium after 60 minutes. However, AC adsorption had not reached equilibrium after 100 minutes. The remediation by AC adsorption had removed an average of 70 % of each herbicide after 100 minutes compared to 14 % by LCM perstraction. The experimental results obtained from liquid-liquid extraction and AC equilibrium studies were used to calculate approximately how many

grams of DBS oil and AquaSorb 2000 would be required to remove 0.5 mmol/L MCPA, 2,4-D or dichlorprop from aqueous solutions. For example, the removal of 0.5 mmol/L MCPA by DBS oil would require a 55 fold increase in the gram quantity needed for remediation compared to the use of activated carbon. It is envisaged that a combined treatment of LCMs and activated carbon may be beneficial. The LCMs can be designed to be target specific (Dalton cut off, hydrophobicity) thereby enhancing the purification process by the activated carbon filters in DWTPs which adsorb a wide range of pollutants. The LCMs could then be easily removed from filter beds by flotation.

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Appendix A

Equations used for HPLC validation

Precision

$$RSD = \frac{\sigma}{\overline{x}} \times 100 \tag{A.1}$$

Where, σ is the standard deviation and $\overline{x}$ is the average calculated from n=6 replicate injections.

Accuracy

$$Accuracy = \frac{C_M}{C_T} \times 100 \tag{A.2}$$

Where, C_M and C_T are the measured and theoretical concentrations respectively.

LOD

$$LOD = \frac{3.3\sigma}{S} \tag{A.3}$$

Where S is the slope of the calibration curve. The standard deviation was obtained from the y-intercepts of the regression lines.

LOQ

$$LOQ = \frac{10\sigma}{S} \tag{A.4}$$

Capacity factor

$$k' = \frac{(t_R - t_0)}{t_0} \tag{A.5}$$

Where t_R is the retention time of the analyte and t_0 is the elution time of the void volume or non-retained components.

Tailing factor

$$T = \frac{a + b}{2a} \tag{A.6}$$

Where T is the tailing factor, a is the peak width, which is measured from the front of the peak to the peak maximum at 5 % from the baseline of the peak height, and b is the peak width measured from the peak maximum to the end of the peak. The measurements described are illustrated in Figure A.1.

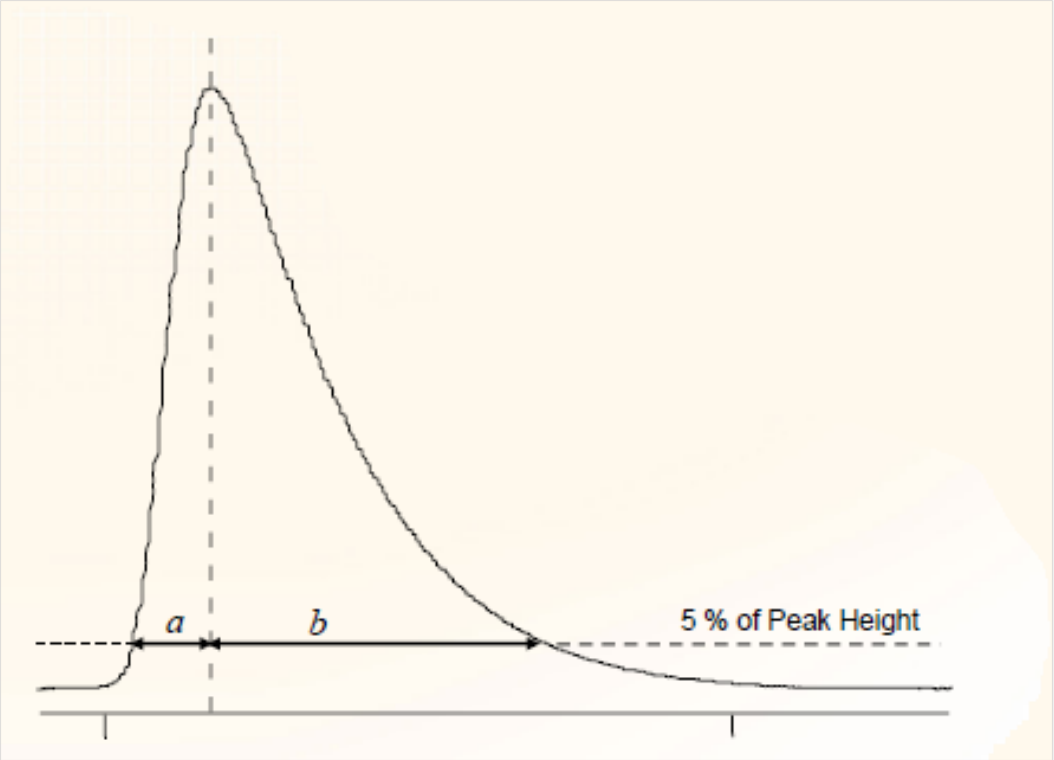


Figure A.1: An example of how tailing factor is calculated based on the U.S. Pharmacopoeia [75].

Theoretical plates

$$N = 16(\frac{t_R}{t_W})^2 \tag{A.7}$$

Appendix B

Supplementary data for Chapter 3

Table B.1: Freundlich equation parameters calculated for MCPA adsorption to AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons at pH 4^b, 4, 6 and 8. (^{b} donates unbuffered)

activated carbon	pH	K_F	n	R^2	SSE	SE
AquaSorb 2000	4^b	1.80	3.41	0.8991	0.0414	0.1018
	4	1.85	2.11	0.9994	0.0181	0.0001
	6	1.43	2.76	0.9993	0.0000	0.0018
	8	0.90	4.73	0.9744	0.0028	0.0263
Norit 1240W	4^b	2.04	2.43	0.6545	0.0002	0.0076
	4	1.49	2.19	0.9798	0.0004	0.0104
	6	1.59	2.27	0.8921	0.0002	0.0065
	8	0.81	3.46	0.9396	0.0063	0.0105
BP2 ColorSorb	4^b	3.40	2.07	0.9800	0.0010	0.0159
	4	2.51	2.99	0.6909	0.0257	0.0802
	6	0.97	6.73	0.2263	0.1414	0.1880
	8	0.73	6.81	0.4347	0.0853	0.1460
Sigma Aldrich C-3014	4^b	1.29	2.10	0.9633	0.0050	0.0345
	4	1.33	3.28	0.9181	0.0002	0.0061
	6	0.84	4.20	0.9958	0.0003	0.0088
	8	0.48	6.25	0.9413	0.0005	0.0116

The activated carbon adsorption capacity order for MCPA (characterised by the Freundlich parameter K_L) for pH 4^b, 4, 6 and 8 was as follows:

pH 4^b:

BP2 ColorSorb > Norit 1240W > AquaSorb 2000 > Sigma Aldrich C-3014

pH 4:

BP2 ColorSorb > AquaSorb 2000 > Norit 1240W > Sigma Aldrich C-3014

pH 6:

BP2 ColorSorb > AquaSorb 2000 > Norit 1240W > Sigma Aldrich C-3014

pH 8:

AquaSorb 2000 > Norit 1240W > BP2 ColorSorb > Sigma Aldrich C-3014

The activated carbon adsorption capacity order for 2,4-D (characterised by the Freundlich parameter K_L) for pH 4^b, 4, 6 and 8 was as follows:

Table B.2: Langmuir equation parameters calculated for MCPA adsorption to AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons at pH 4^b, 4, 6 and 8. (^{b} donates unbuffered)

activated carbon	pH	q_m	K_L	R_L	R^2	SSE	SE
AquaSorb 2000	4^b	1.01	77.13	0.10	0.8824	0.0483	0.1099
	4	0.76	40.91	0.10	0.9992	0.0002	0.0066
	6	0.85	75.79	0.06	0.9992	0.0000	0.0019
	8	0.69	91.56	0.04	0.9607	0.0042	0.0326
Norit 1240W	4^b	1.14	31.05	0.15	0.7678	0.0002	0.0062
	4	0.79	20.68	0.16	0.9976	0.0000	0.0036
	6	0.71	46.22	0.07	0.9904	0.0000	0.0019
	8	0.53	65.45	0.04	0.9972	0.0003	0.0086
BP2 ColorSorb	4^b	1.37	29.08	0.28	0.9407	0.0030	0.0274
	4	0.95	151.82	0.05	0.7637	0.0197	0.0701
	6	0.64	750.30	0.01	0.1704	0.1517	0.1947
	8	0.56	155.37	0.02	0.4332	0.0855	0.1462
Sigma Aldrich C-3014	4^b	0.87	11.04	0.27	0.9081	0.0126	0.0561
	4	0.67	73.73	0.06	0.9542	0.0000	0.0046
	6	0.44	294.31	0.01	0.8865	0.0083	0.0456
	8	0.41	142.53	0.02	0.9787	0.0002	0.0070

Table B.3: Freundlich equation parameters calculated for 2,4-D adsorption to AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons at pH 4^b, 4, 6 and 8. (^{b} donates unbuffered)

activated carbon	pH	K_F	n	R^2	SSE	SE
AquaSorb 2000	4^b	2.02	3.01	0.8930	0.0452	0.1062
	4	2.32	1.76	0.9988	0.0001	0.0056
	6	1.36	2.79	0.9653	0.0071	0.0420
	8	1.25	2.90	0.9729	0.0022	0.0233
Norit 1240W	4^b	1.17	4.22	0.7879	0.0549	0.1172
	4	1.08	2.18	0.9639	0.0000	0.0018
	6	1.59	2.23	0.8765	0.0062	0.0395
	8	0.92	2.86	0.9800	0.0009	0.0146
BP2 ColorSorb	4^b	2.72	2.43	0.5669	0.0198	0.2227
	4	1.88	3.56	0.9470	0.0019	0.0218
	6	1.12	5.69	0.6840	0.0437	0.1045
	8	0.80	6.66	0.7243	0.0401	0.1002
Sigma Aldrich C-3014	4^b	0.85	3.03	0.9185	0.0063	0.0398
	4	0.95	3.05	0.9828	0.0002	0.0066
	6	0.85	4.41	0.9973	0.0000	0.0040
	8	0.54	5.08	0.9959	0.0000	0.0005

Table B.4: Langmuir equation parameters calculated for 2,4-D adsorption to AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons at pH 4^b, 4, 6 and 8. (^{b} donates unbuffered)

activated carbon	pH	q_m	K_L	R_L	R^2	SSE	SE
AquaSorb 2000	4^b	1.07	58.55	0.13	0.8843	0.0488	0.1105
	4	0.75	28.10	0.13	0.9999	0.0000	0.0018
	6	0.68	73.44	0.05	0.9976	0.0005	0.0110
	8	0.58	75.36	0.05	0.9702	0.0024	0.0244
Norit 1240W	4^b	0.84	55.35	0.08	0.8218	0.0462	0.1074
	4	0.59	23.32	0.12	0.8842	0.0000	0.0032
	6	0.74	37.43	0.08	0.9896	0.0005	0.0115
	8	0.64	20.92	0.13	0.9401	0.0026	0.0253
BP2 ColorSorb	4^b	1.34	31.45	0.26	0.5608	0.2011	0.2242
	4	0.68	350.88	0.02	0.9412	0.0021	0.0230
	6	0.72	201.70	0.03	0.6528	0.0480	0.1095
	8	0.63	155.81	0.02	0.7016	0.0434	0.1042
Sigma Aldrich C-3014	4^b	0.61	20.75	0.15	0.6782	0.0250	0.0791
	4	0.68	20.07	0.15	0.8542	0.0015	0.0192
	6	0.67	38.01	0.09	0.9778	0.0005	0.0113
	8	0.37	213.08	0.01	0.9663	0.0000	0.0014

Table B.5: Freundlich equation parameters calculated for dichlorprop adsorption to AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons at pH 4^b, 4, 6 and 8. (^{b} donates unbuffered)

activated carbon	pH	K_F	n	R^2	SSE	SE
AquaSorb 2000	4^b	1.05	4.10	0.9542	0.0094	0.0486
	4	0.96	2.60	0.9982	0.0001	0.0057
	6	1.33	2.77	0.9769	0.0006	0.0122
	8	1.13	3.05	0.9694	0.0030	0.0273
Norit 1240W	4^b	1.37	2.87	0.9556	0.0102	0.0505
	4	0.91	2.20	0.8597	0.0092	0.0479
	6	0.92	2.79	0.9789	0.0035	0.0295
	8	0.83	3.16	0.9698	0.0011	0.0168
BP2 ColorSorb	4^b	2.22	2.96	0.5778	0.0809	0.1422
	4	1.61	4.35	0.9993	0.0001	0.0052
	6	1.22	7.32	0.4935	0.1984	0.2227
	8	0.75	7.21	0.6908	0.0402	0.1003
Sigma Aldrich C-3014	4^b	0.96	2.18	0.9597	0.0027	0.0260
	4	0.74	4.18	0.9658	0.0002	0.0069
	6	0.75	4.05	0.9535	0.0014	0.0019
	8	0.51	5.26	0.9945	0.0002	0.0068

Table B.6: Langmuir equation parameters calculated for dichlorprop adsorption to AquaSorb 2000, Norit 1240W, BP2 ColorSorb and Sigma Aldrich C-3014 activated carbons at pH 4^b, 4, 6 and 8. (^{b} donates unbuffered)

activated carbon	pH	q_m	K_L	R_L	R^2	SSE	SE
AquaSorb 2000	4^b	0.68	148.73	0.03	0.9694	0.0063	0.0397
	4	0.57	36.08	0.09	0.9841	0.0011	0.0168
	6	0.48	137.12	0.03	0.9703	0.0008	0.0138
	8	0.59	71.96	0.05	0.9717	0.0028	0.0263
Norit 1240W	4^b	0.64	128.25	0.03	0.8825	0.0270	0.0821
	4	0.60	13.54	0.15	0.9705	0.0019	0.0220
	6	0.57	44.44	0.07	0.9113	0.0146	0.0604
	8	0.58	24.65	0.11	0.9578	0.0016	0.0198
BP2 ColorSorb	4^b	1.07	58.36	0.16	0.5726	0.0819	0.1431
	4	0.94	153.35	0.05	0.9176	0.0126	0.0561
	6	0.91	290.42	0.02	0.4901	0.1997	0.2235
	8	0.61	163.79	0.02	0.6745	0.0423	0.1029
Sigma Aldrich C-3014	4^b	0.74	8.50	0.28	0.9029	0.0065	0.0403
	4	0.55	44.04	0.07	0.9940	0.0000	0.0029
	6	0.45	100.38	0.03	0.9428	0.0017	0.0207
	8	0.36	205.21	0.01	0.9893	0.0004	0.0096

pH 4^b:

BP2 ColorSorb > AquaSorb 2000 > Norit 1240W > Sigma Aldrich C-3014

pH 4:

BP2 ColorSorb > AquaSorb 2000 > Norit 1240W > Sigma Aldrich C-3014

pH 6:

Norit 1240W > AquaSorb 2000 > BP2 ColorSorb > Sigma Aldrich C-3014

pH 8:

AquaSorb 2000 > Norit 1240W > BP2 ColorSorb > Sigma Aldrich C-3014

The activated carbon adsorption capacity order for dichlorprop (characterised by the Freundlich parameter K_L) for pH 4^b, 4, 6 and 8 was as follows:

pH 4^b:

BP2 ColorSorb > Norit 1240W > AquaSorb 2000 > Sigma Aldrich C-3014

pH 4:

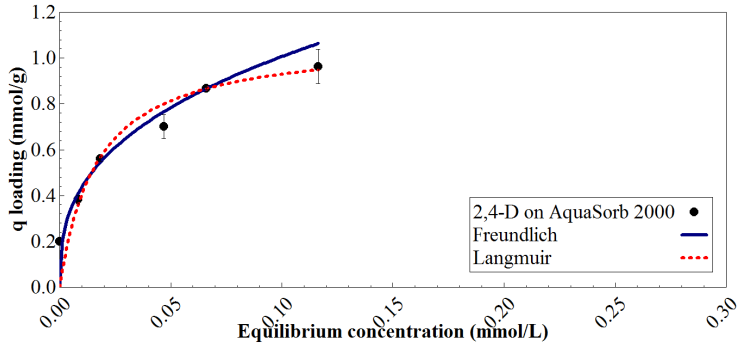
BP2 ColorSorb > AquaSorb 2000 > Norit 1240W > Sigma Aldrich C-3014

pH 6:

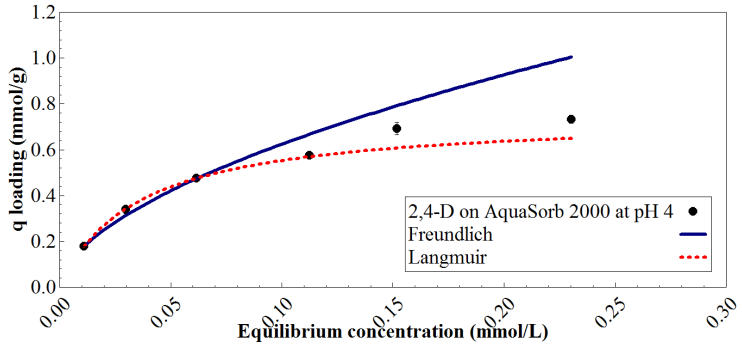
AquaSorb 2000 > BP2 ColorSorb > Norit 1240W > Sigma Aldrich C-3014

pH 8:

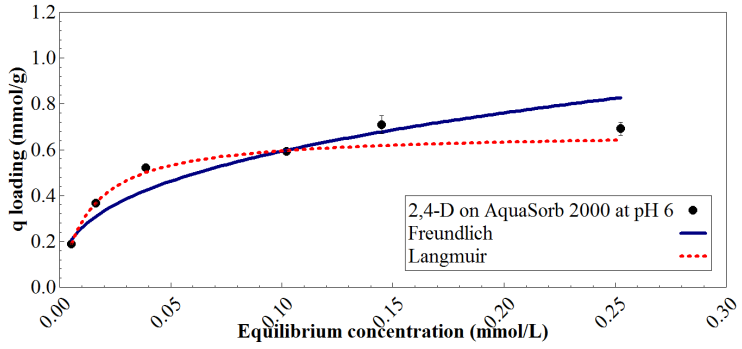
AquaSorb 2000 > Norit 1240W > BP2 ColorSorb > Sigma Aldrich C-3014



(a)



(b)



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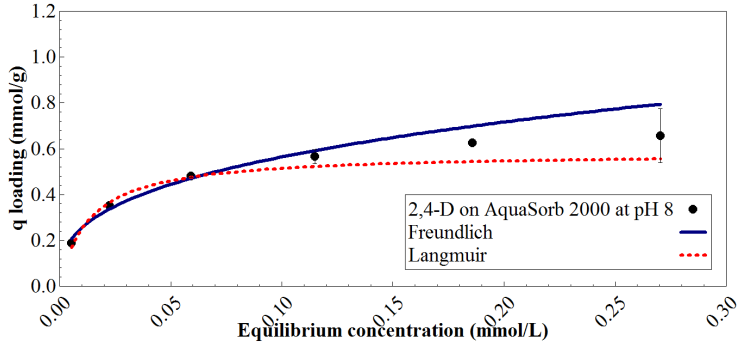
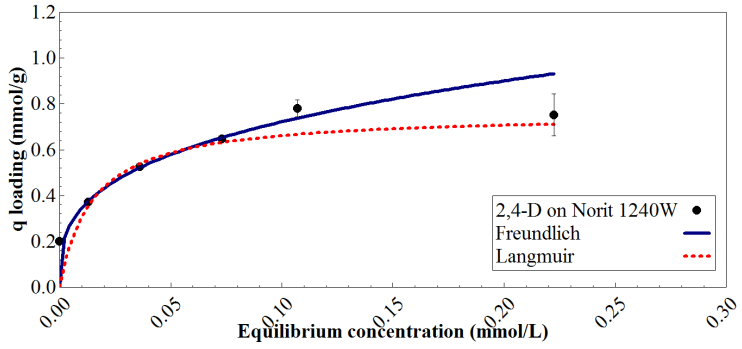
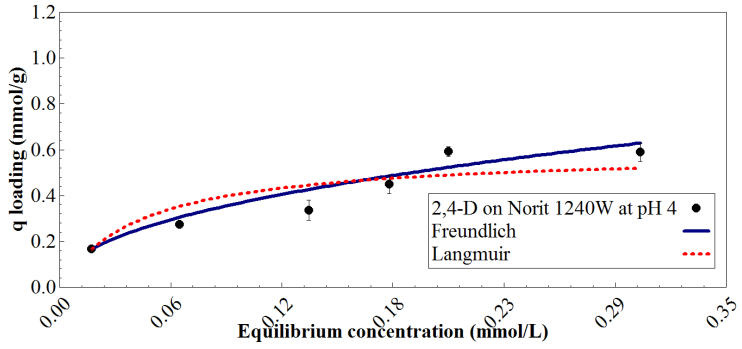


(d)

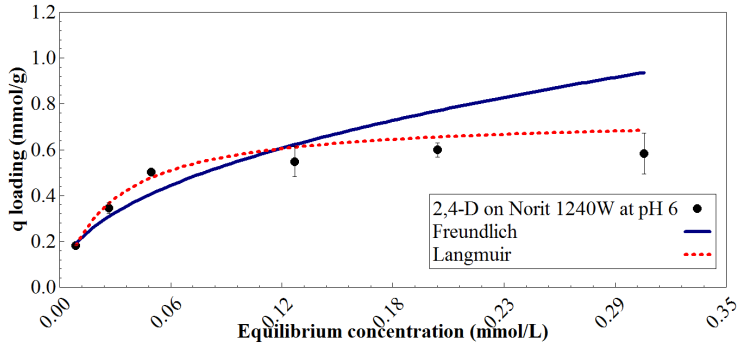
Figure B.1: Freundlich and Langmuir isotherm model fit for 2,4-D adsorption to AquaSorb 2000: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



(a)



(b)



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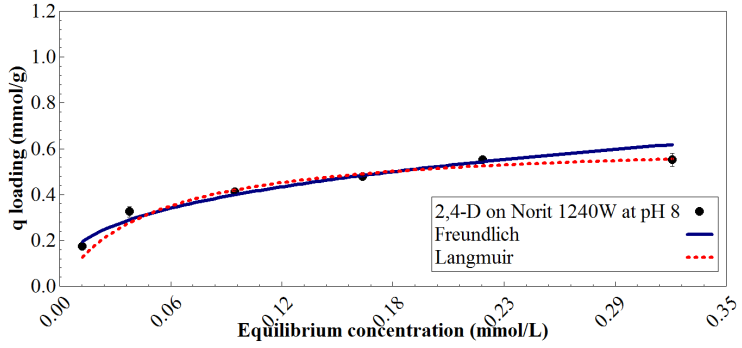
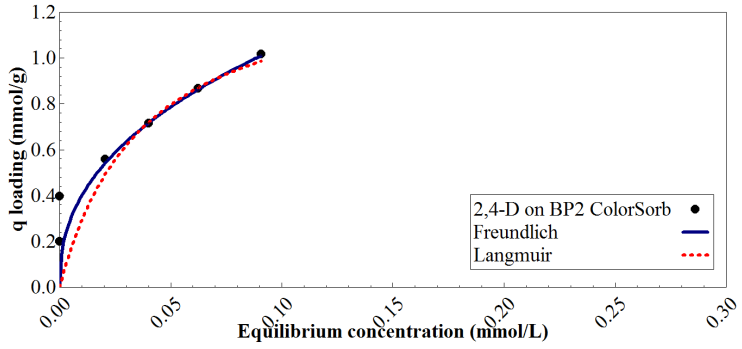
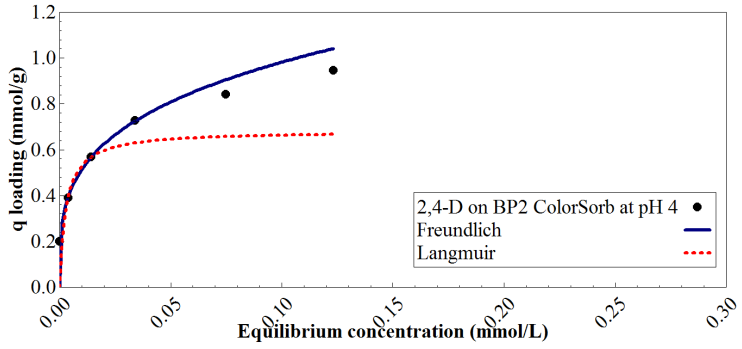


(d)

Figure B.2: Freundlich and Langmuir isotherm model fit for 2,4-D adsorption to Norit 1240W: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



(a)



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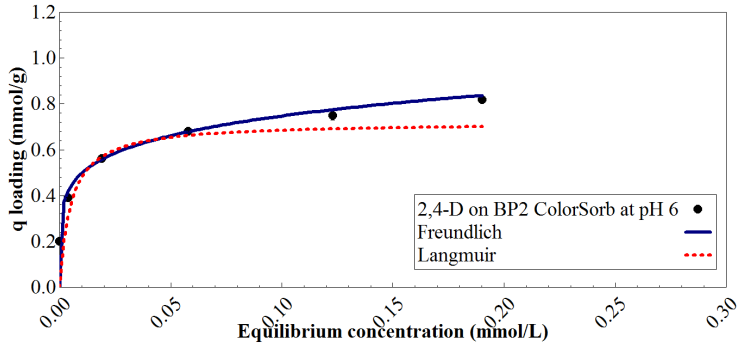

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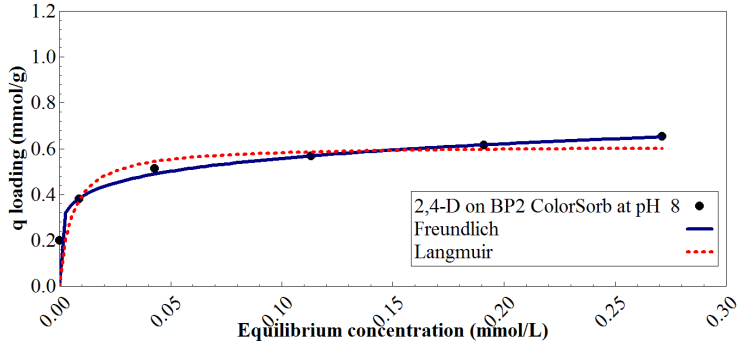
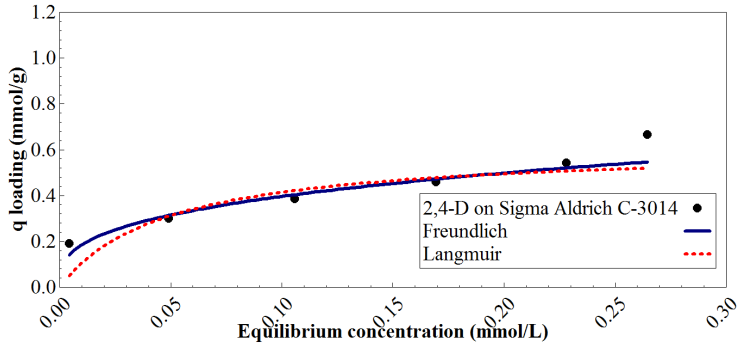
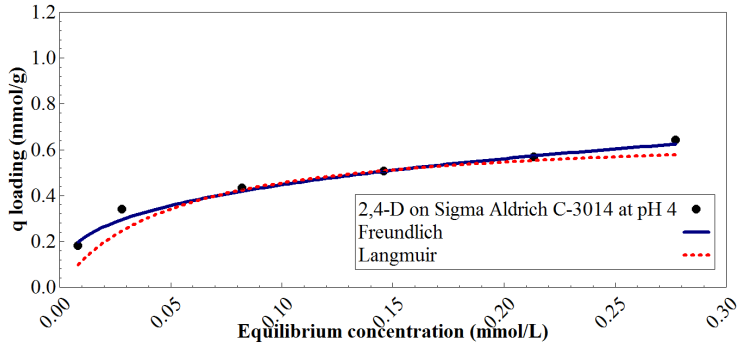


(d)

Figure B.3: Freundlich and Langmuir isotherm model fit for 2,4-D adsorption to BP2 ColorSorb: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



(a)



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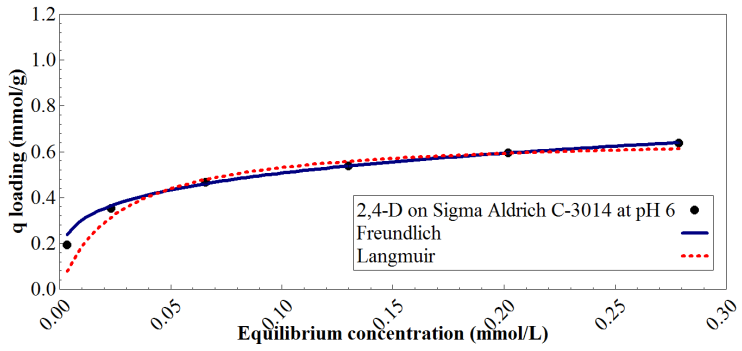

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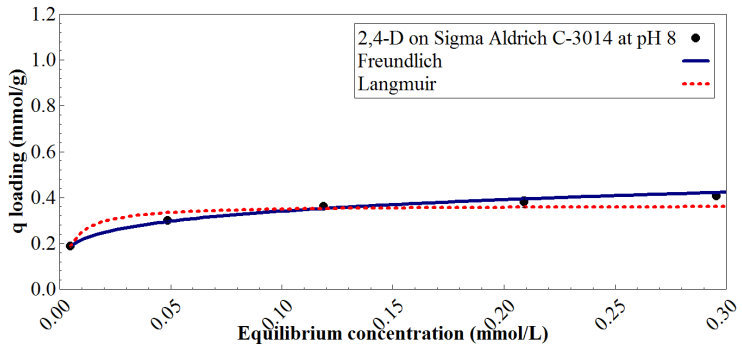
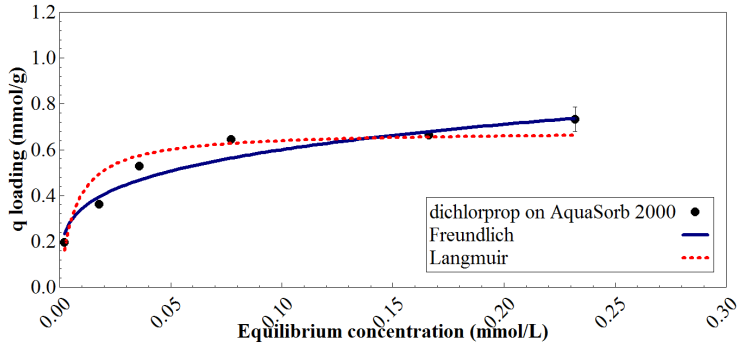
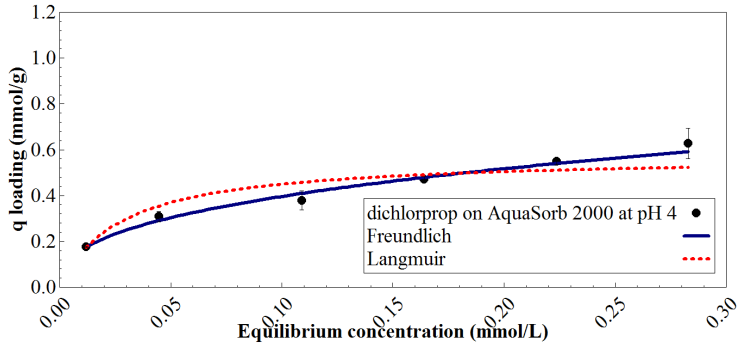


(d)

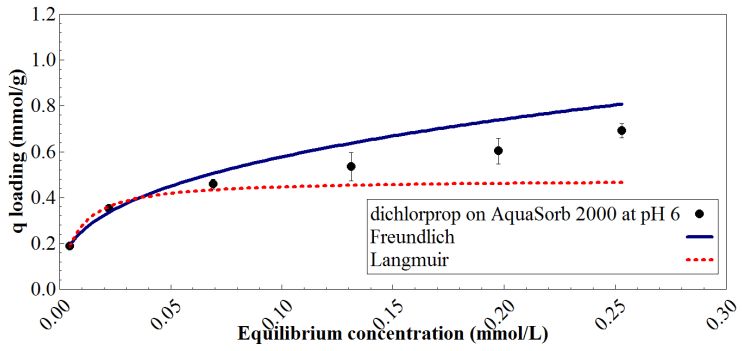
Figure B.4: Freundlich and Langmuir isotherm model fit for 2,4-D adsorption to Sigma Aldrich C-3014: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



(a)



(b)



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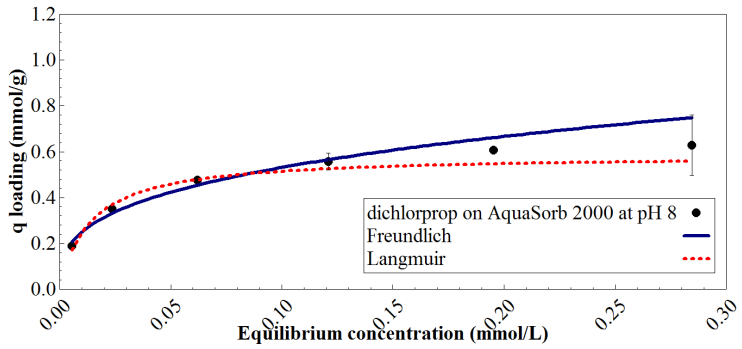
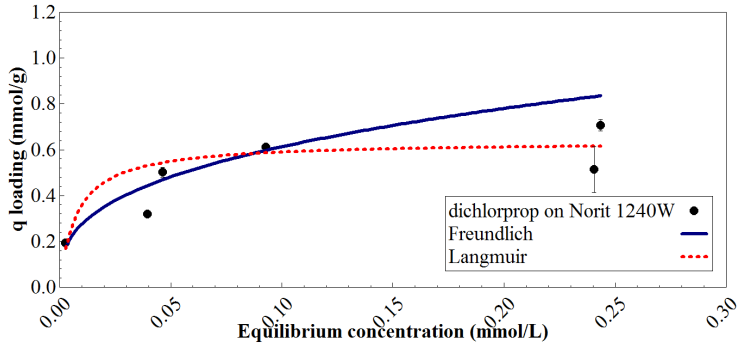
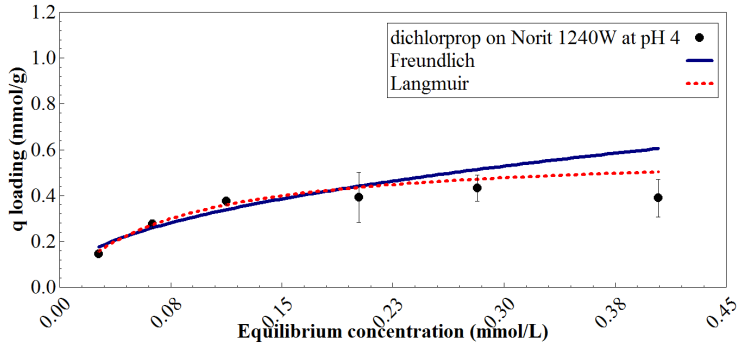


(d)

Figure B.5: Freundlich and Langmuir isotherm model fit for dichlorprop adsorption to AquaSorb 2000: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



(a)



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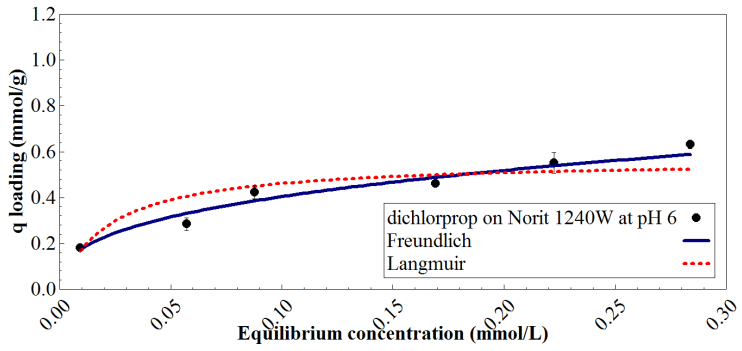

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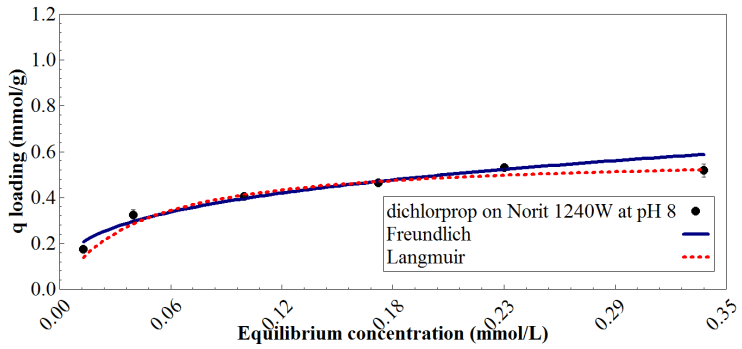
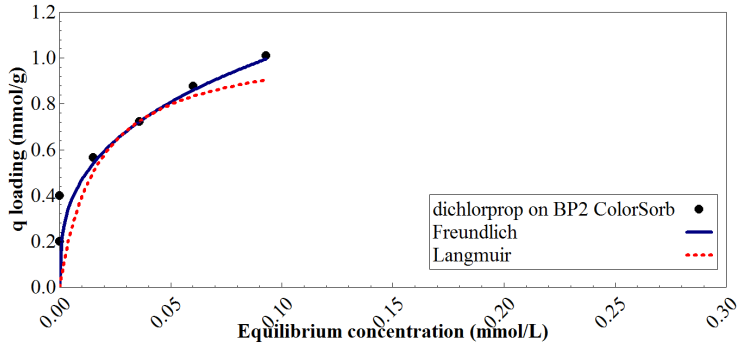
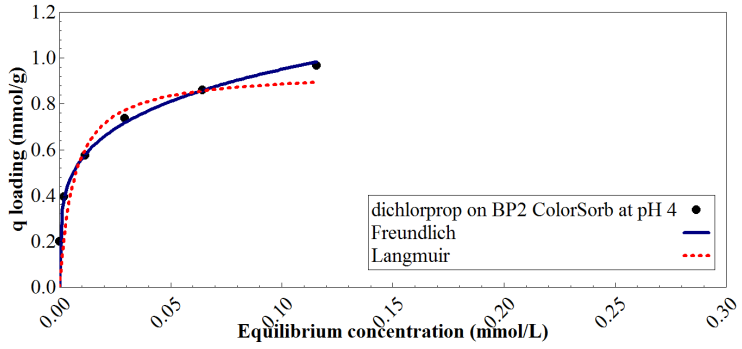


(d)

Figure B.6: Freundlich and Langmuir isotherm model fit for dichlorprop adsorption to Norit 1240W: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



(a)



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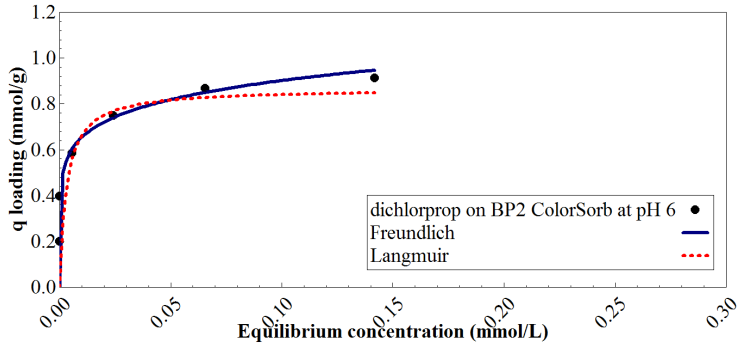

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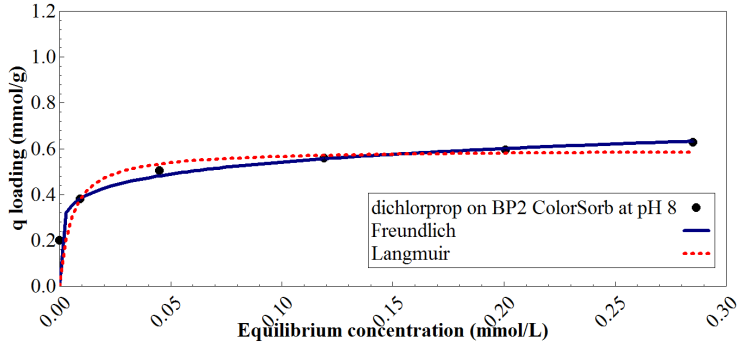
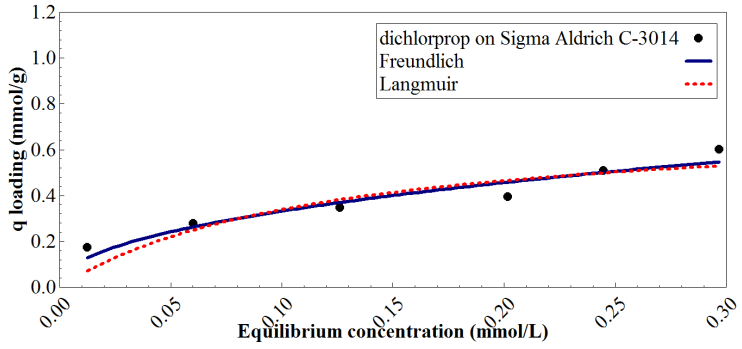
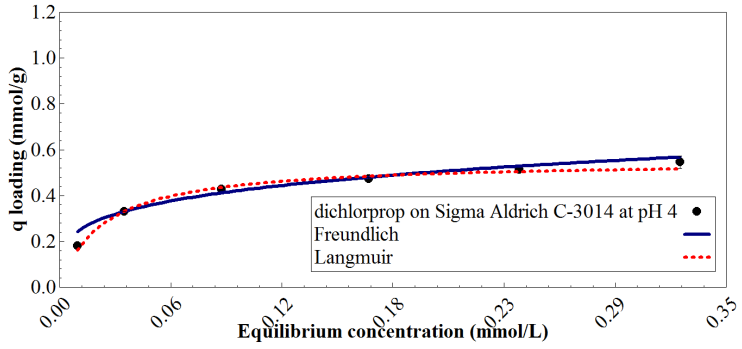


(d)

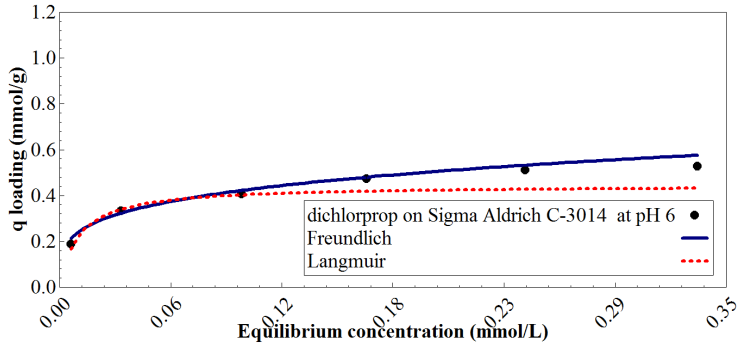
Figure B.7: Freundlich and Langmuir isotherm model fit for dichlorprop adsorption to BP2 Color-Sorb: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .



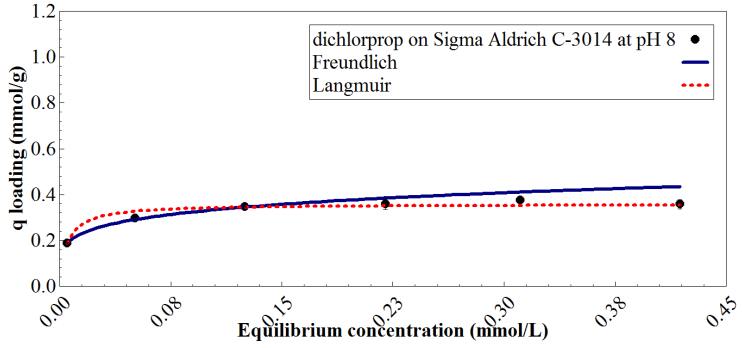
(a)



(b)



(c)



(d)

Figure B.8: Freundlich and Langmuir isotherm model fit for dichlorprop adsorption to Sigma Aldrich C-3014: (a) unadjusted; (b) at pH 4; (c) at pH 6; and (d) at pH 8 .