In-situ Electrochemical Regeneration of Granular Activated Carbon
- Experimental and Theoretical Study Regarding the Treatment Performance of Dye and Pesticides

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by

Harold Ifedayo Oyovwevotu

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Jens Muff

AALBORG UNIVERSITY
DENMARK

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Section of Chemical Engineering
Department of Chemistry and Bioscience
Aalborg University, Esbjerg
Denmark

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Preface

The presented project is a master thesis titled ‘*In-situ Electrochemical Regeneration of Granular Activated Carbon - Experimental and Theoretical Study Regarding the Treatment Performance of Dye and Pesticides*’ written by Harold Ifedayo Oyovwevotu. This work serves as the final written report which contributes towards the Master of Science (M.Sc.) degree in Chemical Engineering at Aalborg University, Esbjerg. This project was written under the guidance and supervision of Jens Muff.

This thesis concerns the combined technological development of both electrochemical and physico-chemical water treatment methods, more specifically the combination of adsorption and electrochemical regeneration. Prior investigation has been carried out regarding the potential of this combinational method, but more research, development and optimisation for feasibility for large scale applications

Due to unforeseen circumstances of COVID-19 and the country’s lockdown, the original aim and approach of this project had to be altered to be completed. More specifically, access to the lab was affected midway through the project and was no longer permitted for the remainder. Thus, it was not possible to fulfil all intended lab experiments and investigations, which caused a change in direction for the experimental section of this project.

Abstract

A range of micropollutants, including several pharmaceuticals and pesticides, are inadequately treated in water treatment plants. With activated carbon, adsorption processes, can be employed as a resolution method to reduce their discharge into aquatic environments. This paper highlights and experimentally investigates the combinational treatment method of adsorption with electrochemical regeneration. Lab scale parameter studies were performed to investigate the various operational factors of the adsorption system, which consisted of temperature, the added carbon amount and adsorption combined with applied electric potential. HGR-AC was utilised in a developed electrochemical batch reactor to determine the removal efficiency of organic contaminants represented with the dye, RNO. With the change from 10 mg HGR-AC to 500 mg HGR-AC, the removal efficiency increased from 42% to 97%. The combined adsorption and applied electric potential also showed to be proficient and improved the degradation process of RNO. Results obtained from published literature were used for the investigation of electrochemical regeneration; through the evaluation of the operational parameters' adjustment: such as the variation in regeneration time, regeneration cycles and current intensity. The found results suggested a dependency on the system's operational conditions used; thus, final results are varied. Five regeneration cycles were the stated maximum number of practical cycles, along with a regeneration time ranging from two to five hours. The highest regeneration efficiency achieved from the published studies was 98%, which used the highest current of 3 A. The information provided in this thesis showed the success rate of electrochemical regeneration through different parameter perspectives, which can further research in this scientific field.

Keywords: Adsorption; Electrochemical Treatment; Activated Carbon; Electrochemical Regeneration; Pesticide Degradation

Abbreviations

AC	Activated Carbon
AO	Anodic Oxidation
AOPs	Advanced Oxidation Processes
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DoE	Design of Experiments
DOM	Dissolved Organic Matter
EC	European Commission
EO	Electrochemical Oxidation
EU	European Union
GAC	Granular Activated Carbon
HGR-AC	HGR-Activated Carbon
HPLC	High Performance Liquid Chromatography
K_{OC}	Soil Adsorption Coefficient
K_{OW}	n-octanol/water Partition Coefficient
N	Nitrogen
NOM	Natural Organic Matter
P	Phosphor
QSAR	Quantitative Structure Activity Relationship
SPE	Solid-Phase Extraction
SS-316	Stainless Steel-316
TOC	Total Organic Carbon
US EPA	United States Environmental Protection Agency
WTPs	Water Treatment Plants
WWTPs	Wastewater Treatment Plants

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Chapter 1

1. Introduction

Over the past decades, the human population has significantly increased, resulting in a greater need for industrial and agricultural applications of pesticides, that has proven vital for human survival and existence. Pesticides has completely revolutionised global society, as it has greatly impacted the agricultural industry through aiding and providing cleaner food production. From societal perspective, the use of pesticides has probably saved countless numbers of people from starvation, disease and nutrient deficiency [1]. However, pesticides in their current form, have adverse side effects including environmental pollution. This problem has become a major global concern, due to the elevated level of pesticides and other micropollutants found in drinking water [2]. Focus has been targeted towards the remediation of these harmful substances from drinking water resources, as their persistence may lead to cancer, organ damage and other severe illnesses [3]. Similar associated forms of micropollutants found in drinking water are caused by the agricultural industry and the use of synthetic chemicals [4].

The presence of micropollutants, such as pesticides, which act as emerging pollutants in the environment, has become a problem of upmost concern due to their toxic and hazardous environmental and human impact. Even though pesticides have shown great benefits, these xenobiotic organic compounds pose an evident potential threat towards the quality of drinking and groundwater resources [2,5]. Their persistence within water resources has caused the shutdown of multiple drinking wells in Denmark and the EU, due to the constant and regular detection of pesticides above limit values [6]. With the low degradability of pesticides, there is a high probability of leaching to occur through the soil into the subsurface which causes the contamination of the groundwater. Pesticide contamination and their introduction to aquatic environments can occur from different sources such as agricultural use, landfills, spraying of private gardens and public areas, market gardens and accidental spills, which are diffuse sources and point sources [7,8].

The current methods used in wastewater treatment plants (WWTPs) are intended for the regulation and elimination of nutrients, such as nitrogen (N) and phosphorous (P), along with the reduction of the present organic content: biological and chemical oxygen demand (BOD) and (COD), and total organic carbon (TOC); through primary, secondary and tertiary treatment technologies. However, for drinking water treatment, these methods are not intended for the elimination of micropollutants, which affects their removal efficiency. Consequently, this has become a big challenge faced by the drinking water treatment industry due to their low concentrations commonly present in water. If unmediated, hazardous health effects such as short- and long-term toxicity along with a rise in antibiotic-resistant genes in bacteria can become a major risk [8].

Adsorption is a commonly used remedial method employed in treatment facilities to remove pesticides from water. One of the most powerful adsorbent materials for this method is granular activated carbon (GAC), due to the material’s large surface area, microporous structure along and increased surface reactivity [3]. Although deemed as a highly efficient adsorbent material, GAC does possess the disadvantage of a limited reactivity lifetime, after which performance then decreases. In untreated water, the dissolved organic matter (DOM) saturates the present active sites on the surface of GAC with irreversibly bound organic contaminants and slowly reduces the adsorption capacity. When the adsorbent reaches the adsorption capacity limit, GAC becomes ineffective and can no longer be used as an adsorbent, usually making it necessary for disposal or replacement. However, the continuous replacement and disposal of exhausted adsorbent material carries an economic cost. A resolution for this challenge is to regenerate the material, such that it can be used for multiple cycles of adsorption and regeneration [9].

Several regeneration techniques have been used for exhausted GAC, which include thermal, chemical and microbial methods. However, these methods are accompanied with limitations such as pore blockage, carbon attrition, high energy consumptions, low regenerative rates and in some circumstances the requirement of a secondary treatment [10,11]. To overcome and avoid such limitations, an electrochemical method was first employed as a regenerative method by *Narbaitz and Cen (1994)*. When the exhausted GAC was placed within opposing electrodes and an electric current is applied, both desorption and degradation of the organic contaminants were observed. With electrochemical regeneration, GAC has reached between 80-95% regeneration compared to other conventional regenerative methods that achieved upto 70% [12,13]. The adsorption amount efficiency after regeneration and increased operating lifetime offered by this technique has sparked further interest in this area.

Nevertheless, there are numerous questions that have been raised regarding adsorption with electrochemical regeneration, such as whether the treatment was conducted directly on the adsorbent surface when an electric current has passed through, does oxidation occur indirectly through the active sites on the adsorbent's surface, or were the compounds and substances oxidised in the bulk liquid? To answer these questions, an in-depth investigation into this process would evidently aid our understanding of the treatment mechanisms entailed. Additionally, it would be also interesting to investigate the effect of various operational parameters, which would highlight the relationship between the applied electric charge and current efficiency, with regards to the pollutants degradation and electrochemical regeneration [14].

1.1. Aim of Thesis

This thesis is focused on the investigation and utilisation of combining the physico-chemical treatment method of adsorption with electrochemical regeneration of GAC, as an improved polishing treatment method for WTPs suitable enough for EU drinking water regulations. The goal of this thesis is to source and devise optimum adsorption operational parameters which can be further used to successfully remove pesticides and organic pollutants, represented by a target-dye, from wastewater and contaminated waters. Thereafter, the intention is steered towards the evaluation of electrochemical regeneration and its operational parameters as an adsorbent media regeneration treatment method for exhausted GAC.

Hence, the aim of work is focused towards determining the optimum operational parameters necessary to obtain sufficiently high, and possibly to increase, the in-situ regeneration efficiency of exhausted GAC, after the treatment of a contaminated water source. During the experimental analysis, different parameters and factors are investigated: the amount of added adsorbent, temperature, applied electric potential. Published literature is then also sourced and utilised to investigate in-situ electrochemical regeneration through the parameters of regeneration time, number of regeneration cycles and current intensity. All these factors combined are to aid in the determination of whether the degradation and regeneration efficiency can be improved through optimisation.

Chapter 2

2. Pesticides in Drinking Water

It is a well-known fact that water quality is an imperative environmental health threat that has been experienced worldwide for decades and is still an active threat to this date. The chemical industry has continuously developed a vast range of pesticides, pharmaceuticals and plastics for the upkeep of the human population. These substances and their degradation products, after use or processing, are usually found in wastewater which then undergoes the required treatment, and potentially ending up in drinking water resources. Pesticides are most commonly introduced into aquatic environments through both point sources and non-point sources of pollution such as agricultural run-off, as well as accidental spills and wastewater discharges [3]. There are various factors which contribute and are dependent on pesticidal pollution:

- The chemical nature of the pesticide
- The physical properties and characteristics of the landscape surface
- The weather conditions which may aid or impede leaching

Regarding pesticides, there are different categories which they can be separated into, dependent on their target pests: herbicides, insecticides, fungicides, and rodenticides. The structure within pesticides are developed to imitate and substitute specific molecules in targeted biological processes; the “mode of action” for a pesticide is specialised and specific towards the targeted pest. However, with the benefits that are associated with pesticides, they have proven to show harmful and toxic effects, with the possibility of being carcinogenic, towards non-targeted organisms such as humans, animals and the environment [15–17].

To reduce the risk of unintentional intoxication of non-targeted organisms, regulators identify hazardous pesticides which will either need to be banned or have limited/restricted use. In Ireland 2013, the department of Agriculture Food and Marine (D.A.F.M 2013) reported on the sustainable use of pesticides, which devises a strategy for pesticidal sustainable use, along with goal objectives, quantifiable measures and timeframes to reduce risks [16,18]. The European Parliament has utilised this report and made as a requirement under the directive 2009/128/EC (EC. 2009) [16,19].

However, with the many preventative legislations and regulators that have been employed for pesticides and their continued use in the agriculture industry, a percentage will undoubtedly reach natural water systems. The mode of transport will most likely be through surface run-off during intense rainfall events, which as a result, emphasises the imperativeness for developing and innovating methods needed for their removal and regulation [3].

2.1. Entry of Pesticides in Water

As previously stated, there have been regulators established to control and limit the use of pesticides to avoid the over-saturation of soil and groundwater, which can lead to negative harmful consequences towards the environment, human and animal life [3,16]. These regulations have been instated to decrease the over-application or misuse of pesticides and other agricultural chemicals. It is possible for processes such as evaporation, wind erosion and drift to transport pesticidal particles into the atmosphere, from which, can fall as rain or snow to contaminate lakes and rivers. Groundwater is easily susceptible to contamination through the excessive use of agricultural chemicals onto porous soil, giving an easy access to shallow water tables, followed by further percolation into the groundwater [3].

Pesticides can also enter water resources through surface run-off, erosion and leaching. Naturally when water flows across the land surface, through either rainfall or irrigation, it will always flow downhill or where gravity leads it until reaching an end-barrier or stagnant area or begins to percolate into the soil. In consideration to surface run-off theory, the aid of wind and water erosion of the soil allows the pesticidal particulates and residues to also be carried to surrounding aquatic environments. This even applies to insoluble pesticides and pesticides with a high affinity to soil adsorption [17,20]. All the possible pesticidal movements within the hydrological cycle is shown in Figure 2.1.

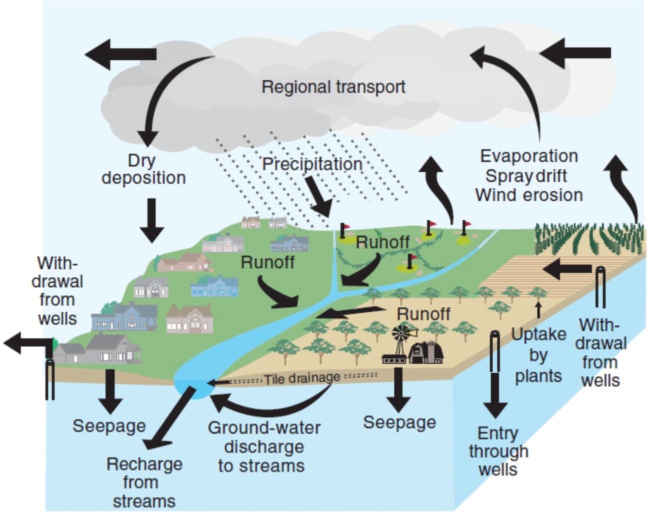


Figure 2.1: Pesticide Movement in the Hydrological Cycle [141]

As mentioned earlier, there are two ways in which pesticides can enter aquatic environments: from point sources or non-point sources as shown in Figure 2.2. Point sources are usually small areas which contains high concentrations of pesticides such as tanks, containers, or accidental spills. Non-point sources are broader areas which contain residues of pesticides that may be transported via surface run-off [20].

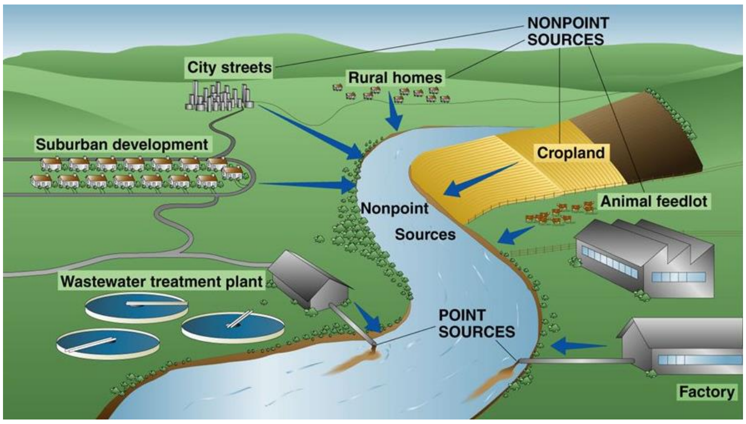


Figure 2.2: Point and Non-point Sources of Pesticide Pollution [142]

2.2. Pesticides in EU Drinking Water Supplies

Obtaining data with regards to the occurrence of specific pesticides located in the environment is somewhat challenging. Due to pesticides containing a complex, intricate and diverse group of chemical compounds, each requiring the necessary analytical test method specific for that pesticide or group of pesticides. When testing drinking water sources, pesticides are in one of the chemical parameters that are tested, but the pesticides most likely to be present in the given sample are required monitoring. The pesticides that are required for screening are provided by the relevant water supply authority. Which in turn, means that water treatment plants (WTPs) and WWTPs do not routinely test for all pesticides. Thus, further suggests data regarding this topic is limited to an extent [20,21].

In Europe, pesticides are used in abundance across the continent and have been commonly detected in freshwater resources. Transportation of these pesticides is through diffuse pathways from surface run-off. Regarding surface waters, the European Environmental Agency (EEA) has uncovered that a percentage of freshwater bodies located in the UK are at risk of diffuse pollution from agricultural pesticides [16,22]. In Germany, the groundwater was known to contain leached pollution of pesticides exceeding the recommended quality limits. In early 1990's, 28.3% of the available water sources were tested for pesticides, 9.7% of the samples contained pesticidal residues above the limit. In the late 1990's, 27.6% of water sources contained detectable residues, from which 8.6% exceeded the drinking water limit of 0.1 µg L^{-1}. Even though, less than 10% of the groundwater bodies showed exceeding pesticidal limits, there are signs of declination in pesticidal pollution [23].

2.3. Characteristics of Common Pesticides

It has been estimated that there are currently over 1200 pesticides that are available in the market within the EU. Of those pesticides, the most commonly used pesticides are atrazine, MCPA, mecoprop-P (MCPP), glyphosate, and 2,4-D, along with newly found pesticides that have been showing a reoccurrence in WTPs.

2.3.1. Atrazine

One of the most globally used herbicides used is a triazine herbicide, named atrazine. Even though this herbicide is abundantly used in the United States, in 2004 it was banned of use within the EU and is under review by the US EP. Atrazine is also listed in the EC list of priority substances, (EC. 2001), and is known to be persistent within the environment [24,25]. Depending on the surrounding conditions, the half-life of atrazine ranges from days to years and is not a biodegradable pesticide with endocrine-disrupting capabilities [25]. Studies have shown that the removal of atrazine through adsorption with activated carbon was significantly affected by the surface chemistry of the adsorbent; adsorbents treated with another chemical such as HCl and N_2 showed to positively affect the removal process [26,27].

2.3.2. MCPA

MCPA is a pesticide that is used for controlling the growth of weeds for cereals and grasslands. MCPA is a chlorophenoxy acid compound that acts as a selective systemic hormone type herbicide which is absorbed by leaves and roots. The guidelines for drinking water quality instated by WHO has classed MCPA as an important substance due to possessing a photolytic half-life ranging from 20 to 24 days, in aerobic conditions. The water-insoluble, non-volatile MCPA acid has a shown a moderate to low-toxicity to birds and other animals [28]. However, when tested for toxicity towards mammals and freshwater fish, it was established that MCPA was slightly toxic to mammals and highly toxic to fish within short-term exposure [29,30]. Removal of MCPA onto activated carbon proved to be pH dependent - increase in pH is associated with a decrease in adsorption [31].

2.3.3. Glyphosate

One of the most used pesticides in the world is known as glyphosate which is a non-selective herbicide. The high usage of glyphosate is due to being the active ingredient in the common pesticide “Roundup” [32]. Glyphosate is highly water soluble and adsorbs strongly to surface soil, as a result there is a decreased likelihood for glyphosate to percolate towards groundwater. Nevertheless, there is still the possibility of glyphosate surface water contamination through the transportation of residues adsorbed to soil particles suspended in run-off water. When present in surface water, glyphosate has shown to be persistent and resists degradation processes such as hydrolysis and aqueous photolysis. With long-term exposure, there is a high risk of damage to the kidneys and reproductive organs. [33,34]. Glyphosate removal by activated carbon seemed to be greatly impacted by concentration and adsorbent dose. It was also discovered that a higher removal rate and greater removal efficiencies were achieved at elevated temperatures of 50 °C [35].

2.3.4. Mecoprop-P (MCPP)

MCPP is another chlorophenoxy herbicide which is used against annual and perennial broadleaf weeds. MCPP is highly water soluble, suggesting low potential to adsorb to soil particulates. Therefore, the herbicide leaches into both groundwater and surface water without difficulty. The US EPA has classed MCPP as slightly toxic after short-term exposure [36]. A study conducted by *Oh and Tuovinen (1994)* showed, when combined in a mixture with 2,4-D, after adsorption, MCPP had persistent residual substances; meanwhile, 2,4-D was completely degraded [37].

2.3.5. 2,4-D

The pesticide 2,4-D is a chlorophenoxy acid and is widely used as a broadleaf herbicide. Within the presence of natural water, the pesticide has shown moderate stability and photostability with a high solubility in water, suggesting a strong persistence in the environment. In aerobic conditions, the half-life ranges from one to several weeks, whereas in anaerobic conditions, the half-life of 2,4-D can surpass 120 days [38]. *Aksu and Kabasakal (2007)* investigated the uptake of 2,4-D onto powdered activated carbon, and their results showed the highest yielded uptake capacity of 333.33 mg g^{-1} was gained at 25 °C with an initial pH of 2 [39].

2.3.6. BAM

BAM is a pesticide metabolite of the herbicides chlorthiamid (2,6- dichlorothiobenzamide) and dichlobenil (2,6-dichlorobenzonitrile), this pesticide has proven to be exceedingly persistent in soil and groundwater, which has made it one of the most frequently detected groundwater micropollutants. There is currently no physico-chemical treatment methods employed for the removal of BAM in WTPs ; therefore, if concentrations exceed above the legal regulatory standard limit of 0.1 µg L^{-1}, it poses a problem towards the stability and quality of drinking water production, especially for areas which are dependent on groundwater for drinking water. During the 1990’s, BAM was in 22% of water samples taken from Danish water supply wells, with the mean and median concentration being 0.318 and 0.040 µg L^{-1}, respectively. The highest detected concentration was 560 µg L^{-1}. A couple years later, in 2002, a study stated that BAM was in 34 – 38% of small Danish water supply wells, with 14 µg L^{-1} being the highest recorded [40–42].

2.3.7. N,N-Dimethylsulfamide (DMS)

DMS is a recent upcoming, newly identified degradation product of the fungicide tolyfluanide, which is an active ingredient in fungicides used for fruit and wine culturing since approximately 1974. The first detections of DMS were sourced in 2006, southern

Germany with found concentrations ranging between 0.1 – 1 µg L^{-1}. Currently employed water treatment processes such as bank filtration or adsorption with activated carbon have proven to not effectively remove DMS. Ozonisation is a method which converts DMS into N-nitrosodimethylamine, which is highly carcinogenic and regulated at very low levels in drinking water 10 ng L^{-1}. As a result, ozonisation of natural waters containing DMS is critical for the treatment process, even when DMS concentrations in raw water are low [43].

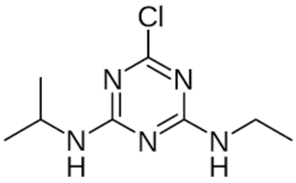
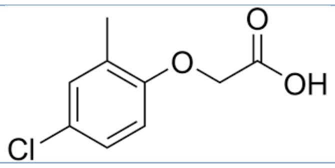
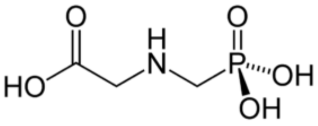
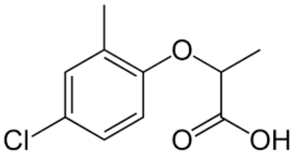
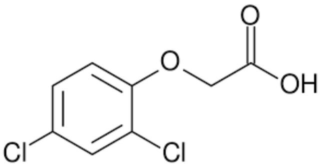
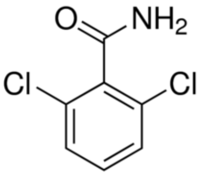
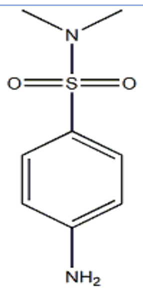
2.3.8. Structures and Properties

The physico-chemical properties and structures of the aforementioned pesticides are shown in Table 2.1 and Table 2.2.

Table 2.1: Physico-chemical Properties of Pesticides

Pesticide Name	Molecular Weight [g M^{-1}]	Water Solubility (at 20 °C) [mg L^{-1}]	Density [g cm^{-3}]	Log(K_{OW})	Log(K_{OC})
Atrazine	215.68	30 - 35	1.19	2.82	2.35
MCPA	200.62	29390	1.21	2.52	1.47
Glyphosate	169.07	10500	1.70	-4.77	-0.64
MCPP	214.64	250000	1.30	2.94	1.69
2,4-D	221.04	24300	1.57	2.62	1.47
BAM	190.03	2700	1.44	0.90	1.66
DMS	200.26	11680	1.30	0.55	1.43

Table 2.2: Chemical Formula and Structure of Pesticides

Pesticide Name	IUPAC Name	Chemical Formula	Structure
Atrazine	6-chloro-*N*-ethyl-*N'*-isopropyl-1,3,5-triazine-2,4-diamine	$C_8H_{14}ClN_5$	
MCPA	4-chloro-o-tolyoxyacetic acid	$C_9H_9ClO_3$	
Glyphosate	N-(phosphonomethyl)-glycin	$C_3H_8NO_5P$	
MCPP	2-(4-chloro-2-methylphenoxy)propanoic acid	$C_{10}H_{11}ClO_3$	
2,4-D	(2,4-dichlorophenoxy)acetic acid	$C_8H_6Cl_2O_3$	
BAM	2,6-Dichlorobenzamide	$C_7H_5Cl_2NO$	
DMS	N',N'-Dimethylsulfanilamide	$C_8H_{12}N_2O_2S$	

Chapter 3

3. Water Treatment Methods

With the continuous increase in industrial and agricultural growth, and environmental legislation becoming stricter in recent years; there has been a growing interest towards environmental pollution and its remediation, as the impact of pollution towards global water quality is detrimental to human and environmental health. Due to this, water treatment methods and technologies have been created and established as a combatant to the problem. With the high urgency and demand that is placed on the innovation and optimisation of water treatment methods, from an economical and industrial perspective, the most important aspect that should be considered is operational costs. Hence, the treatment method should be sufficiently effective as well as economical. There are also various parameters that should be considered when designing treatment methods, such as the organic and inorganic constituents within the water, the pH, and the flowrate of the water etc. [44,45].

3.1. Adsorption

The process of adsorption can be described as a mass transfer process involving the adhesion and accumulation of one or more molecular components from either a gas, liquid or dissolved solid on the surface of an adsorbent material. The material adsorbing the substances is referred to as the *"adsorbent"*, while the substances that are being adsorbed are called *"adsorbates"*. In the context of water treatment with adsorption, adsorption onto activated carbon is a common water purification technique due to its strong ability to remove organic substances even at low concentrations. This phenomenon arises due to that attractive forces that occur between the adsorbate molecule and the adsorbent surface. The attractive forces that take place can be van der Waals, intermolecular, electrostatic or as a result to chemical interactions. The attractive forces that take place during physical adsorption are van der Waals and intermolecular but because of the attractive forces' weak nature, physical adsorption can be separated through the application of heat or by reducing the pressure of the material being adsorbed to make it possible for the formation of a multilayer upon the adsorbent's surface. Another type of adsorption is known as chemical adsorption, which occurs through the chemical interaction between the reacting species involved, as a result a monolayer is formed, as shown in Figure 3.1. Unlike physical adsorption, chemical adsorption uses electrostatic interactions or strong covalent bonds, which increase the strength of the process, making it somewhat permanent or irreversible [46–48].

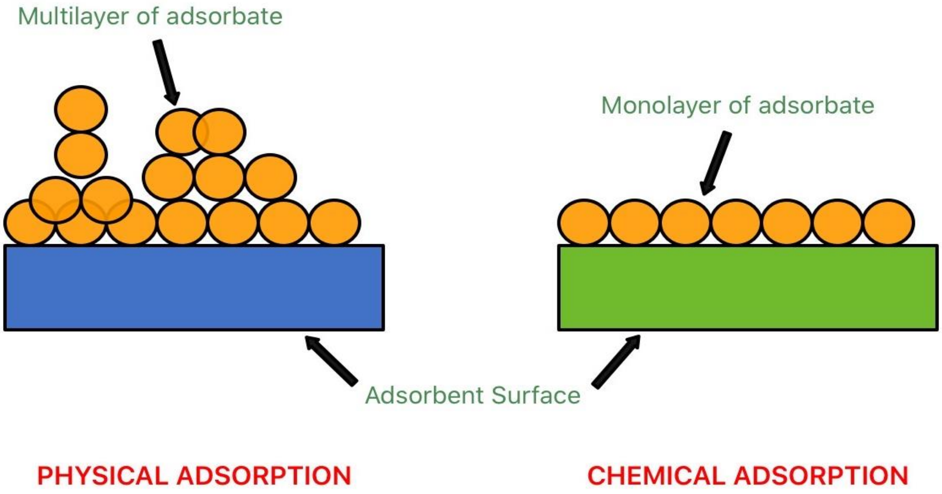


Figure 3.1: Surface Activity of Physical and Chemical Adsorption [48]

There are multiple factors that affect the performance of the adsorbent: the equilibrium nature, the stoichiometric capacity of the solid and the adsorption rate. On the other hand, factors such as the porosity, surface area and structure of the adsorbent, along with the diffusion of the solute impact the kinetics involved in the adsorption process. Adsorption kinetics are greatly important to approximately determine the time needed to acquire maximum adsorbent loading. In the adsorption process, when the rate of adsorption equates to the rate of desorption, the adsorption equilibrium can be depicted and defined. Adsorbents can be characterised based on the amount of solute accumulated on their surface during the process. Adsorption isotherms are use calculate the maximum loading capacity of solute on surface of the adsorbent, they are defined as the variation of the loading capacity of the adsorbent surface in equilibrium with the concentration of solute in solution at constant temperature. As a result, determination of the time required to reach adsorption equilibrium is vital for calculating the adsorption isotherms. Contributing factors such as the surface morphology of the adsorbent, diffusion coefficient and the nature of the solute, all have an influence on the adsorption isotherms. Within liquid-phase adsorption, the Freundlich, Langmuir and Temkin isotherm models apply [46,47,49].

3.1.1. Freundlich Isotherm

The Freundlich adsorption isotherm is utilised for liquid phase adsorption onto solid surface characterised with heterogeneous energy distribution. This isotherm model defines the surface heterogeneity and the exponential distribution of the available active sites on the adsorbent's surface and their energies. In other terms, it applies to heterogeneous surfaces and assumes multi-layer formation. The model assumes that adsorption will increase infinitely as the adsorbate concentration increases [50,51]. The Freundlich isotherm in non-linear form is shown in equation 3-1.

$$\boldsymbol{q_e = K_F C_e^{\frac{1}{n}}} \tag{3-1}$$

Where,

q_e is the amount of adsorbate adsorbed onto the adsorbent at equilibrium (mg g^{-1})

K_F refers to the adsorption capacity (L mg^{-1})

C_e is the adsorbate concentration at equilibrium (mg L^{-1})

$\frac{1}{n}$ is the adsorption Freundlich intensity parameter

The linear expression of this isotherm is achieved by taking the logarithms of equation 3-1. The linear model is shown in equation 3-2.

$$\boldsymbol{\log q_e = \log K_F + \frac{1}{n} \log C_e} \tag{3-2}$$

By plotting $\log q_e$ against $\log C_e$, a straight line is given; the slope and the intercept of the straight line can be used to approximate and determine the constants needed for the Freundlich equation [50,51].

3.1.2. Langmuir Isotherm

The Langmuir adsorption isotherm assumes, regarding the adsorbent material, that the surface energy distribution is homogeneous, and is used to quantify and contrast the adsorptive capacity of different adsorbents. This model describes the adsorption rate, which is proportional to the fluid phase concentration and the active sites on the adsorbent. In other terms, the model assumes that a monolayer will form on a uniform surface and that there are no interactions between adsorbates [50,51]. The non-linear formula for the Langmuir model is shown in equation 3-3:

$$\boldsymbol{q_e = q_m \frac{K_L C_e}{1+K_L C_e}} \tag{3-3}$$

Where,

q_e represents the amount of adsorbate adsorbed onto the adsorbent at equilibrium (mg g^{-1})
q_m represents the maximum adsorbed loading onto the adsorbent (mg g^{-1})
C_e is the adsorbate concentration at equilibrium (mg L^{-1})
K_L represents the associated Langmuir constant related to adsorption capacity (L mg^{-1})

The Langmuir isotherm shown in equation 3-3 can be linearised by rearrangement. The linearised isotherm formula is shown in equation 3-4.

$$\boldsymbol{\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}} \tag{3-4}$$

A method to acquire the Langmuir constants is to plot $\frac{1}{q_e}$ vs. $\frac{1}{C_e}$. As previously mentioned, the performance of adsorbents is characterised by the amount of solute accumulated on their surface, also referred to as their loading capacity, q_e. Even though the loading capacity is vital towards the performance of an adsorbent, it is influenced by factors such as pH, particle size and temperature [50,51].

3.1.3. Temkin Isotherm

The Temkin adsorption isotherm explains the behavior of adsorption systems on heterogenous surfaces, and is usually used in the expression shown in equation 3-5:

$$\boldsymbol{q_e = \frac{RT}{b} \ln{(A_T C_e)}} \tag{3-5}$$

The model takes into account the effects of the indirect adsorption interactions within the process; it is also assumed that the heat of adsorption (ΔH_{ads}) of all molecules in the layer decreases linearly as a result of the increase in surface coverage. The Temkin isotherm can be expressed in the linear form shown in equation 3-6:

$$\boldsymbol{q_e = \frac{RT}{b} lnA_T + \frac{RT}{b} lnC_e} \quad [3\text{-}6]$$

Where,

$$\boldsymbol{B = \frac{RT}{b}} \quad [3\text{-}7]$$

Then,

$$\boldsymbol{q_e = BlnA_T + BlnC_e} \quad [3\text{-}8]$$

A_T represents the Temkin isotherm equilibrium constant (L g^{-1})

b represents the Temkin isotherm constant

R is the universal gas constant (8.314 J mol·K^{-1})

T is Temperature (298 K)

B is the constant related to the heat of sorption (J mol^{-1}) [51,52]

3.1.4. Rate Order Models

3.1.4.1. Pseudo-First Order

In the late 1890's, Lagergren developed a somewhat first order rate equation, which was deemed as the first kinetics-rate equation for the sorption of liquid-solid systems based on the solid's adsorption capacity [53]. This pseudo-first order model assumes the adsorption rate at any specific time is proportional to the difference between the amount of adsorbate adsorbed at equilibrium and at the specified time. The Langregen equation, has become one of the most common rate equations for measuring the sorption of a solute from a liquid solution, which allowed for the equation to be classed as a pseudo-first order model due to the equation possessing the ability to differentiate between a kinetics equation based on concentration and the adsorption capacity of an adsorbent [54]. The differential pseudo-first order equation is shown in equation 3-9:

$$\boldsymbol{\frac{dq_t}{dt} = k_1(q_e - q_t)} \quad [3\text{-}9]$$

Equation 3-10 is then created when equation 3-9 is integrated for boundary conditions such as t = 0 to t = t and $q_t = 0$ and $q_t = q_t$.

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \qquad [3\text{-}10]$$

Where,

q_e is the amount of adsorbate loaded onto the adsorbent at equilibrium (mg g^{-1})

q_t is the amount of adsorbate loaded onto the adsorbent at time, t (mg g^{-1})

k is the equilibrium rate constant of pseudo-first sorption (min^{-1})

The integrated equation 3-10 can be rearranged to obtain a linear form, as displayed in equation 3-11:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad [3\text{-}11]$$

3.1.4.2. Pseudo-Second Order

In 1999, Ho and McKay stated that the sorption capacity is proportional to the number of active sites on the sorbent, which prompted the kinetic law of pseudo-second law to be rewritten as the differential equation shown in equation 3-12:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad [3\text{-}12]$$

Where k_2 is the rate constant of pseudo-second order sorption [g mg^{-1} min^{-1}]. Due to the boundary conditions: t = 0 to t = t and $q_t = 0$ and $q_t = q_t$, equation 3-12 requires to be integrated:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad [3\text{-}13]$$

Equation 3-13 can then be rearranged into a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad [3\text{-}14]$$

Or a non-linear form:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \qquad [3\text{-}15]$$

3.1.5. Adsorption Capacity and Affecting Parameters

With regards to the adsorption process, optimising the adsorption rate and adsorption capacity is an important goal to achieve an efficient system. There are many contributing factors that can aid or hinder the adsorption process such pH, particle size, temperature, surface interaction and characterization; understanding the influence of those parameters is vital [55].

3.1.5.1. Particle Size

The adsorption capacity of an adsorbent can be affected by the particle size of the material: the adsorption capacity increases with the decrease in particle size. This is because the specific surface area increases with the decrease of particle size, moreover, increasing the adsorption capacity. A study conducted by *Mohan et al. (2002)*, investigated how the adsorbent's particle size affected the degradation rate of crystal violet dye. Supporting the particle size theory mentioned previously, the results yielded an increase in the removal rate of the dye with decreasing the adsorbent's particle size. Better results were also observed and obtained from the use of powdered adsorbent compared to the granular version [56]. Another paper written by *Walker and Weatherly (1997)* studied the performance of GAC within a fixed bed reactor for acid dyes removal. The results showed there was a greater chance of obtaining a lower effective diffusivity for an adsorbent with smaller particle sizes. This decrease in diffusivity was attributed to the large size of the dye molecule and the micro-pore structure found in granular activated carbon [57].

3.1.5.2. Temperature

With temperature as an influencing adsorption parameter, there are multiple studies that have been conducted where dyes have been used as target contaminants. The previously mentioned study, *Mohan et al. (2002)*, also investigated the impact of varied temperature towards the adsorption process. Their results showed that the adsorption capacity for the removal of dyes increased with the increase in temperature. The increased temperature caused an improved rate of intra-particle diffusion of the adsorbate which could be a reason for their obtained results. Another possible reason to support their findings, is the increased temperature aided the breakdown of the thin layer of adsorbate molecules on the surface of adsorbent that promoted further mass transfer through intra particle diffusion [56]. The removal of acid violet 17 through adsorption and how the process was affected with temperatures ranging between 30 to 60 °C was used studied by *Vijayalakshmi et al. (2011)*. Similar to the previous study, the adsorption capacity increased with the increase in temperature; as already stated, increased temperatures promote intra-particle diffusion which allows for mass transfer operation onto porous particles like activated carbon. Nevertheless, it is not the same for every case and the opposite effect may be observed. As for adsorption systems comprised of weak electrostatic interactions, elevated temperatures can break them down. This suggests the significance of how temperature influences the adsorption process depends on the type of attractive forces between the adsorbent surface and adsorbate, which differs with each system [58].

3.1.5.3. pH

With regards to water treatment, pH-levels play an important role in treatment plants, particularly when treating coloured wastewater. As dyes are used to simulate organic contaminants and pollutants within water, their removal and the effect of pH has been investigated by numerous researchers. In terms of surface charge and dyes, the dyes can be categorised as either anionic or cationic. Anionic dyes possess a negative charge and favourably to attach to cationic surface, these types of dyes prefer acidic conditions. Whereas cationic dyes are attracted to anionic surfaces and are favourable in an alkaline environment [59].

Pavan et al. (2008) investigated the influence of pH towards the adsorption and removal of a cationic dye: methylene blue. The experiments shown that the rate of adsorption increases when the contaminated water was in an alkaline pH range. When in an acidic pH range, a lower adsorption rate was obtained due to the excess amount of H^+ ions that would compete for adsorption sites with the cations contained in the dye. This suggests increasing the amount of negatively charged sites and reducing the number of positively charged sites improves cationic dye removal in a basic pH range; it also suggests that it will be the opposite for anionic dyes [60]. Two studies, *Brown et al. (2004a)* and *Brown et al. (2004b)*, were conducted to investigate the removal of atrazine and crystal violet dye with Nyex® 100 as the absorbent material. They were both tested at different pH levels, 3 and 7, and yielded no significant changes in results. This suggest the influence of pH towards the adsorption capacity is dependent on the type of adsorbate/classification of dye, as they show varied behaviour during removal [61,62].

3.1.5.4. *Surface Interaction*

With the development of new adsorbents, it is very important to understand the surface chemistry and their behavioural interactions in various environments. Since activated carbon can be created from a various source of waste materials, there will be different substance characteristics and behavioural interactions for each specific AC, depending on the source material and method of activation. The different possible characteristics of AC include pore structure, surface charge and the presence of functional groups which significantly influence adsorption capacity and time [63,64]. An overall conceptual diagram of this notion is displayed in Figure 3.2, where it shows the possible adsorption mechanisms that can be considered through surface interactions between a carbonaceous material and inorganic nitrogen contaminants as an example [65].

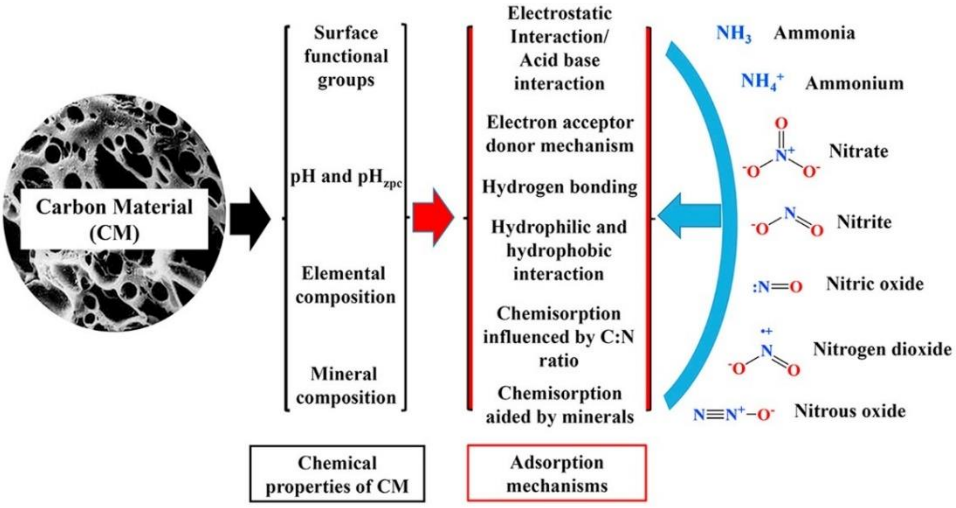


Figure 3.2: Conceptual Diagram of Carbon Material's Surface Interactions with Inorganic Nitrogen Contaminants [65]

Hartono et al. (2009) treated graphite with sulfuric acid to observe the adsorption capacity, surface behaviour and influence of pH. With sulfuric treatment, the adsorption capacity increased; the maximum adsorption capacity for the treated graphite using Langmuir adsorption isotherm was found to be 50 mg g^{-1} greater than untreated graphite. After sulfuric treatment, acidic conditions gave better results for adsorption rates [66]. Other investigations: *Castilla (2004)* and *Castilla et al. (2004)*, reported that the presence of carboxyl and carbonyls groups aid in the development of surface charge and hydrophobicity. The studies also stated, an increase of surface oxygen can help reduce the hydrophobicity of activated carbons [67,68].

3.1.5.5. Surface Characterisation

Another parameter that significantly influences the adsorption rate and adsorption capacity is the surface characterisation of the adsorbent material. Surface characterisation involves various parameters such as porosity, specific surface area, density and pore volume etc. With porosity, the number of pores, shape and size greatly impact the adsorption rate [69]. The available classification of pore sizes that are associated adsorbent pores are shown in Table 3.1.

Table 3.1: IUPAC Classification of Pore Sizes

Pore Classification	Pore Width [nm]
Ultramicropores	< 0.7
Supermicropores	0.7 ~ 2
Micropores	< 2
Mesopores	2 ~ 50
Macropores	> 50

The specific surface area helps determine adsorption capacity. Between the pore size classifications, micropores usually take the largest percentage of internal surface of the activated carbon and contribute to most of the total pore volume. Meanwhile, mesopores and macropores along with the substance's remaining non-porous surface represent the external surface as illustrated in Figure 3.3. Even though, adsorption prefers to occur in the micropores, the meso- and macropores are also vital to the process, as they serve as a pathway for the adsorbate to reach micropores [70].

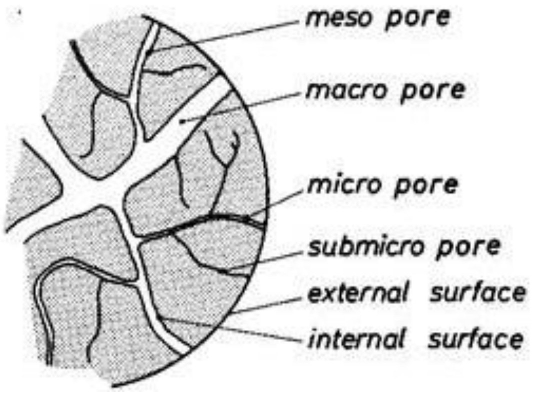


Figure 3.3: Illustration of Porous Structure of Granular Adsorbent [70]

McGuire (1978) conducted an investigation with two types of activated carbons to observe their influence towards the adsorption of pollutants. Regarding the activated carbons, the specific surface areas and pore diameters were 1100 and 650 m^2 g^{-1}, and 3.4 and 5.5 nm, respectively [71]. For adsorption, the specific surface of an adsorbent is an important parameter to obtain high adsorption capacity. A determination method for specific surface area is known as the Brunauer, Emmet and Teller (BET) method, there is also documented use of this method to determine the mono-layer adsorptive capacity by *Ruthven (1984)* and *Ruthven (2006)* [72].

3.1.6. Activated Carbon in Water Treatment

Activated carbon (AC) is the most widely used adsorbent material in water treatment and is used for the removal of organic contaminants along with taste- and odour-compounds, synthetic organic chemicals (pesticides, biocides, herbicides), phenolic compounds and cyanobacterial compounds [73]. AC is a processed form of carbon which is produced from porous media from natural sources such as wood, coal, coconut shells or peat. Under a thermal controlled condition, these carbonaceous materials are transformed into a porous structure with a large surface area, ranging between 500 – 2500 m^2 g^{-1}, possessing a high affinity for organic compounds [74,75]. AC can be classified based on the types of pores within its structure: micro-pores (<2 nm), meso-pores (>2 nm to <50 nm), macro-pores (>50 nm) [76,77]. There are two available forms in which activated carbon can be used: powdered (PAC) or granular (GAC). The difference between the two types of AC, mainly refers to the particle size and shape of which the AC is found; PAC usually has a particle diameter less than 100 µm and GAC ranges between 0.5 to 2.5 mm. Even though, there is a noticeable difference between the particle diameter of AC, both types essentially have similar adsorption properties [64,78–80].

3.1.6.1. Powdered Activated Carbon (PAC)

Due to PAC's inability to be recovered or regenerated, the use of AC-type is associated with a high carbon usage or dosage rate. Compared to GAC, PAC is generally cheaper and can be used to control the seasonal occurrences of pesticides in aquatic environments. Some facilities keep an on-site supply of PAC for emergency control of spikes and silages from municipal and industrial wastewater discharges and agricultural run-off. The advantage of

PAC's low capital cost can be outweighed by its applicability; PAC is limited to the use of low concentrations of organic contaminants due to rapid contact time [81–83].

3.1.6.2. *Granular Activated Carbon (GAC)*

Compared to PAC, GAC has a relatively larger particle size. Due to this and other factors such as high adsorption capacity, selectivity, ability to withstand thermal regeneration and resistance to attrition losses, GAC is more desirable for continuous adsorption processes. In usual circumstances, GAC is employed in a filter contained in a fix-bed reactor, through which water flows downwards through the filter. As a filter, the accumulation of particulates is a common occurrence, which may require periodic backwashing [84,85].

3.1.6.3. *Preparation of Activated Carbon*

Activated carbon can be produced from a wide range of waste materials, the most commonly used materials for commercial carbons are wood, coal, lignite, coconut shells and peat. It is also common for those commercial carbons to undergo an activation process to produce activated carbon. The two main types of activation processes are physical- and chemical-activation [64]. An overall schematic of how carbon materials undergo both types of activation is shown in Figure 3.4 [86].

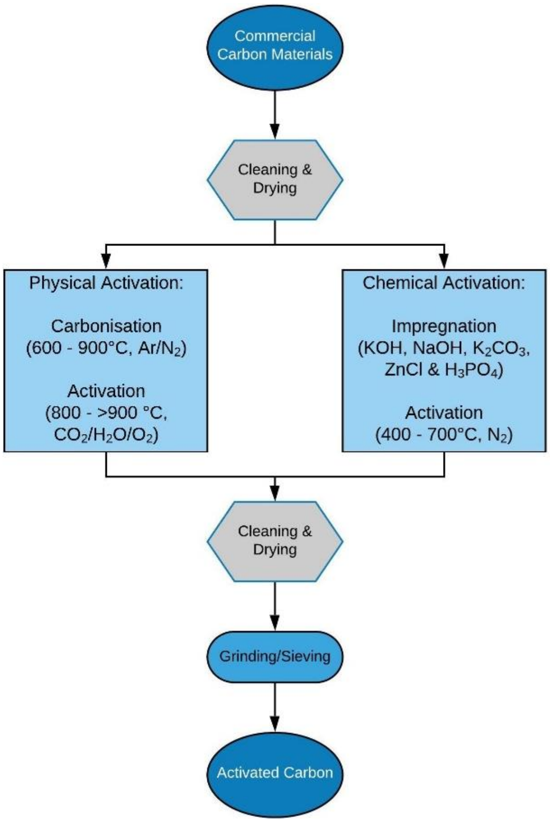


Figure 3.4: Overall Schematic of the Activation of Activated Carbon [86]

3.1.6.3.1. Physical Activation

One of the main activation processes to make activated carbon, is physical activation which follows a three-step process:

- The initial material undergoes oxidation to change the material’s chemical composition.
- Carbonisation of the oxidised material is conducted in inert argon (Ar) or nitrogen (N_2), to eliminate present volatile substances, which produces a carbonic mass possessing a primary pore structure.
- The primary pore structure may be too limiting or small to be used as an efficient adsorbent. Further activation with carbon dioxide or steam increases the number of pores and enlarges the micropores earlier produced during carbonisation by extracting carbon atoms from the pore wall. Thus, creating a new porosity for the material [64,87].

Activation of the carbonic material can be aided with carbon dioxide, steam or molecular oxygen. With carbon dioxide, the activation process is an endothermic reaction shown in reaction 3-1. The steam gasification reaction, “burns out” the available carbon as a combustion reaction but also follows an endothermic pattern as shown in reaction 3-2 [64]:

$$\boldsymbol{C + CO_2 \rightleftarrows 2CO} \tag{3-1}$$

$$\boldsymbol{C + H_2O \rightleftarrows CO + H_2} \tag{3-2}$$

Unlike carbon dioxide, activation with molecular oxygen is a highly exothermic reaction. It gives no enhancement to the porosity because the molecular oxygen reacts and consumes the carbon. These reactions are favourable to react at 600 and >900 °C to form carbon dioxide and carbon monoxide, respectively [64]. The reactions are shown in reaction 3-3 and 3-4:

$$\boldsymbol{2C_f + O_2 \rightleftarrows 2CO} \tag{3-3}$$

$$\boldsymbol{C_f + O_2 \rightleftarrows CO_2} \tag{3-4}$$

C_f represents a carbon atom which is free from bonding with surface complexes, therefore available to react with an oxygen molecule. Physical activation is most commonly used in the production of GAC [64].

3.1.6.3.2. Chemical Activation

The other main type of carbon activation is performed chemically, which produces activated carbons by mixing a ligneous material, usually wood, with a chemical agent. After which, the mixture is then carbonised. In comparison with physical activation, chemical activation requires considerably lower temperatures ranging between 400 and 700 °C, and produces higher final carbon yields. Phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH) and zinc chloride solution ($ZnCl_2$) are commonly used chemicals used for this type of activation, due to the advantage that these chemicals can be recovered and recycled after the activation process [87]. In the chemical activation process, the chemical agents penetrate the surface of the biomass, triggering the biomass structure to enlarge, swell and open the cellulose structure, creating the porosity for the substance. The biomass is then dried in an oven and activated at elevated temperatures ranging between 400 to 700 °C in N_2. After which, the chemical agents are refluxed away with diluted mineral acid. This type of activation is utilised in the formation of PAC [87,88].

3.1.7. Adsorption of Pesticides and Herbicides

Within the environment, the soil adsorption coefficient (K_{OC}) can be reimagined as a numerical indicator for the mobility of pesticides, but to fully comprehend the adsorption of pesticides to soil, the pesticide’s half-life must also be considered. K_{OC} is a measure of a chemical’s tendency to bind to soils; regarding this project, it represents the adsorption of pesticides onto the soil. However, this measure is corrected by the organic matter within the soil to provide a single representation for the specified pesticides. As a result, K_{OC} values can significantly vary depending factors such as soil type, soil pH, the acid-base properties of the pesticide and the type of organic matter within the soil. Regarding K_{OC} values, the larger the value, the stronger the pesticide will bind to the soil and decreases the probability of leeching. The half-life of pesticides may also vary based on the moisture and temperature of the soil, along with other factors. The half-life of non-persistent pesticides usually range from 30 or less days, moderate-lasting pesticides have half-lives between 30 to 99 days, and persistent pesticides possess a half-life greater than 100 days [89,90].

The n-octanol/water partition coefficient (K_{OW}), in retrospect to pesticides, is defined as a measure of the pesticide's hydrophobicity and concentration in two unmixed liquids: octanol and water. K_{OW} values are unitless and are usually expressed as log(K_{OW}), which is an indicator of a pesticide's tendency to adsorb to soil and living organism. This measure is generally inversely related to water solubility, and is a useful parameter to aid with the prediction of a pesticide's distribution in various environments such as water, biota, air, soil, etc. Pesticides possessing high log(K_{OW}) have an increased tendency to adsorb to the organic matter within soils and sediments because of their low affinity with water. Pesticides and other substances with exceedingly high log(K_{OW}) values: greater than 4.5; have the ability to bio-concentrate in living organisms, which has made this parameter necessary for screening tests [91–93].

With the amount of micropollutants remaining in aquatic environments after treatment, it has become an impertinent concern and an expensive process for WTPs and environmental agencies to experimentally determine and remediate each micropollutants; due to the great amount of micropollutants, added with the possibility of continuous newly introduced substances. To reduce experimental work and costs, quantitative structure activity relationship (QSAR) models are employed to predict the removal of micropollutants in water treatment processes such as membrane filtration, ozonation and adsorption; as not all experimental data is available to determine micropollutant removal efficiency. With activated carbon filtration as the removal method for pesticides, QSAR models have been previously used. Through improvements from the early stages of QSAR models which were based on force attractions and H-bond donor/acceptor interactions, removal models could not have been created and used accurately based on previously mentioned characteristics, along with K_{OW} and K_{OC} values solely. Which prompted, current QSAR models to include parameters more related to the adsorption mechanisms. Previous literatures have stated, solute properties including solute charge/polarisablity, hydrophobicity, size and surface characteristics (functional groups) all influence the adsorption of organics onto activated carbon [94].

There have been attempts and experimentation in the creation of implementing physico-chemical parameters of the system into QSAR models to predict the adsorption of the solute. However, with the vast number of different solutes that can included in the dataset, the prediction accuracy of the model is improved by the classification of the solutes into groups based on their properties. In turn, the applicability of the QSAR model is limited to specific groups as a result. Selecting the dependent variable for the QSAR model is crucial, as it should be a representative of the adsorption system; thus, aid the determination in removal efficiency. From previous published literature, the dependent variables used in models for the prediction of equilibrium solute removal have been: (i) The Freundlich capacity constant ($Log\ K_F$); (ii) The adsorbed amount (q_e) in equilibrium with the solution concentration (C_e); and the water/carbon partitioning constant ($Log\ q_e /C_e;\ Log\ K_D$). Even though, there have been advances in QSAR model development, improvements are always useful. Previous models could only explain for the solute removal by one specific carbon type, other properties such as pore size and distribution, surface tension and characteristics should also be incorporated, as they have influence towards the adsorption process. Another limitation is the measured removal from ultrapure water: model water does not fully represent natural waters which contain complex mixtures of natural organic matter (NOM) along with their standard water properties, as they would also affect the adsorption system [94].

Without the use of QSAR models, and regarding the removal of pesticides from contaminated waters, activated carbon produced from a variety of agricultural residues through steam activation was used to test the removal efficiency of bromopropylate (BP) pesticide. The yielded results showed that the greatest obtained maximum adsorption capacity for the AC adsorbents produced from corn cob, olive kernel, soya stalks and rapeseed stalks were 7.9×10^{-2}, 12.3×10^{-2}, 11.6×10^{-2} and 18.9×10^{-2} mmol L^{-1}. From this study, all the ACs had a removal efficiency of BP ranging between 90 to 100% [95]. Another study conducted by *Djilani et al. (2012)* used lignocellulosic derived ACs for the removal of organic pollutants: o-nitrophenol and p-nitrotoluene. The removal efficiency of the pollutants ranged from 70 to 90%, and the necessary time that was acquired to obtain adsorption equilibrium was between 75 and 135 minutes [96].

AC was also used to investigate its removal ability towards common pesticides: 2,4-D and bentazon, at different concentration levels. The obtained removal efficiency for 2,4-D decreased from 98.4 to 85.4% when the initial concentration increased from 50 to 300 mg L^{-1}. Bentazon also experienced a decrease in removal efficiency, when the initial concentration increased from 25 to 250 mg L^{-1}, but at a more drastic rate with 96.5% dropping to 61.6%. This furthers suggests that the initial concentration also plays a key role for the removal efficiency of pesticides. The obtained maximum adsorption capacities for 2,4-D and bentazon from this study were 168.03 mg g^{-1} and 100.95 mg g^{-1}, respectively [97].

3.2. Electrochemical Processes

One of the main aspects of this project is to investigate the capabilities and parameters of electrochemical regeneration of GAC; understanding the foundation of electrochemistry is fundamental. Electrochemistry involves the chemical phenomena associated with charge separation; leading to electron transference that can occur within a solution (homogeneously) or on the surface of electrodes (heterogeneously). In other terms, electrochemistry consists of chemical reactions, in which electrons are transferred between an electron conductor (metallic electrodes) and an ionic conductor (the electrolyte) within a solution [98,99]. This electron transference leads to electrochemical reactions which further lead to oxidation or reduction reactions. In this scenario, oxidation depicts an electron transfer from the species within the electrolyte to the electrode; in other terms, an increase in the oxidative state of the atom, ion or molecule. Whereas, reduction is the inverse, involving a decrease in the oxidative state of the atom, ion or molecule through the donation of electrons from the electrode to the species with the electrolyte [98,100].

The apparatus where electrochemical reactions occur is known as the electrochemical cell. Within this cell, oxidation takes places at the anode while reduction occurs at the cathode. A current from an external source can be applied and passed through the cell, which can be adjusted and utilised for any system. By placing electrodes in an electrolyte, the electrical current path is completed, allowing the migration of ions through the electrolyte [98,100].

Michael Faraday was a scientist who greatly contributed to the study of electrochemistry and electromagnetism. He investigated the relationship between the amount of applied electricity passed through the solution and amount of metal deposited on the electrodes. From his research, the data can be expressed in the form of two laws:

- “The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.
- The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance [100].”

It can be understood the protocol for the first law is achieved from a constant current/electric level, at different values, being passed through an electrolyte, then measuring the amount of deposited material on the electrode at different time periods. Thus, the increase in applied electricity, would amount to an increase of material deposited at the electrode. Faraday's findings for the second law can be verified by passing the same applied electrical current through different solutions. The assumptions of the two laws can then be combined in an mathematical formula as shown equation 3-5 [101,102]:

$$\boldsymbol{m = \frac{QM}{nF}} \tag{3-5}$$

Where,

m is the amount of substance reacted at the electrode (g)
Q is the quantity of charge at the electrode (C)
n is the amount of electrons
F is Faraday's constant (96485 C mol^{-1})
M is the molar mass of the substance (g mol^{-1})

To determine the total charge, Q, that is used in the reaction, it is the multiplied measure of the applied current, *I (A)*, and the time passed, *t (s)*, as shown in equation 3-6. However, regarding electrochemical reactions, there is the possibility for the fluctuation in current. Thus, the charge passed through the cell is the integral of current over time, as portrayed in equation 3-7. Substituting equation 3-6 into equation 3-5, the original displayed equation is re-written as equation 3-8 [101,102]:

$$\boldsymbol{Q = It} \tag{3-6}$$

$$\boldsymbol{Q = \int I\, dt} \tag{3-7}$$

$$\boldsymbol{m = \frac{It}{nF}} \tag{3-8}$$

3.2.1. Electrochemical Oxidation

In the past two decades, electrochemical oxidation (EO) has become a promising advanced oxidation process (AOP) for the degradation of organic pollutants, with the constant development and innovation of new technologies. This process is also used for inorganic pollutants, toxic biodegradable organics and even heavy metallic particulates contained within wastewater. Since the late 1900's, much research into electrode materials and the fundamentals of the degradation process has been made alongside investigations of the technology's applicability to treat an abundance of different contaminants and pollutants. These methods have been directed towards wastewater treatment, with many published reviews and papers on the utilisation and mechanisms of EO. Along with wind power, nuclear power and other emerging power technologies have focused to develop and promote lower power costs, making electrochemical methods in the treatment of wastewater a great advantage [103–105]. With the vast amount of available information on EO, compared with other AOPs, research targeted towards the degradation of pesticides is rather scarce.

Another leading benefit for EO in relation to other AOPs, is that no chemicals are required for this treatment process, as the sole reactant added to the system are electrons. Relative to hydroxyl radicals (·OH) and the EO of organic pollutants, degradation occurs through hydroxyl radicals generated from the oxidation of water, as shown in reaction 3-5. A simplified reaction mechanism between hydroxyl radicals and organic pollutants (R) are displayed in reaction 3-6 [103,104].

$$\boldsymbol{H_2O \rightarrow \cdot OH + H^+ + e^-} \qquad [3\text{-}5]$$

$$\boldsymbol{\cdot OH + R \rightarrow \cdot R + H_2O} \qquad [3\text{-}6]$$

In relation to water treatment, EO of pollutants can be oxidised through either direct or indirect oxidation on the electrodes. Direct oxidation refers to direct electron transfer on the anode surface, whereas indirect oxidation is mediated by various electro-generated oxidising agents such as hydroxyl radicals, persulfate ($S_2O_8^{2-}$) and hydrogen peroxide (H_2O_2) etc. [103,104].

3.2.2. Direct and Indirect Oxidation

Regarding EO, through direct electron transfer, organic contaminants are oxidised and adsorbed on the anode surface, without the addition of any substances other than the electrons. As a result of this process, electrons can be also referred to as a "clean reagent". For indirect oxidation, the organic contaminants in the water are oxidised immediately with the aid of electrochemically generated oxidising agents such as hydroxyl radicals, persulfate

($S_2O_8^{2-}$) and hydrogen peroxide (H_2O_2) [106]. An introduction to electrochemical oxidation mechanisms is presented in Appendix I. An example of an indirect EO mediated by hydroxyl radicals generated through the electrolysis of water is shown reaction 3-5 and reaction 3-6. The mechanisms involved in direct and indirect oxidation are shown in Figure 3.5

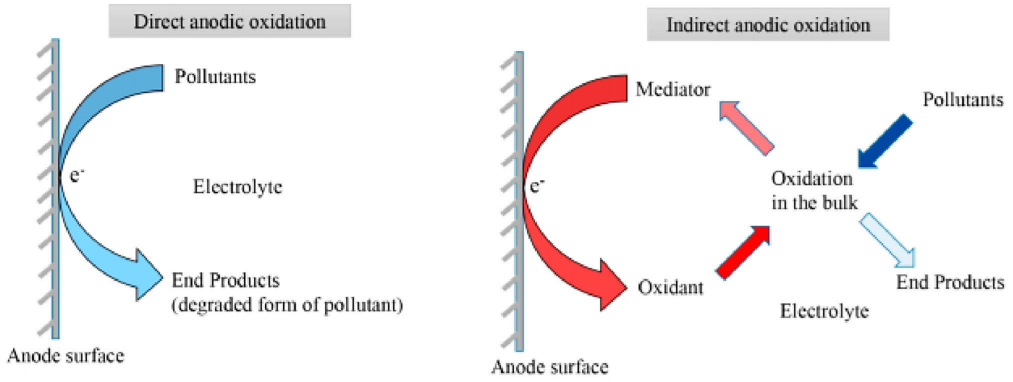


Figure 3.5: Mechanisms for Direct and Indirect Anodic Oxidation [143]

3.3. The Regeneration Process

Regeneration is viewed as a vital and necessary process when an adsorbent has been exhausted, as it becomes expensive for the continuous purchase of new adsorbent materials. In some cases, the adsorbent material is also limited, meaning low availability in large quantities. For adsorbent regeneration, it is commonly performed by changing the conditions within the adsorbent to bring about a lower equilibrium loading capacity, by increasing the temperature or decreasing the partial pressure. With consideration from the economic aspect, an adsorbent is deemed effective if it can be easily regenerated and reused numerous of times without any negative effects hindering its performance. There have been various methods utilised for the regeneration of exhausted adsorbents loaded with organic contaminants: thermal, wet air, chemical and electrochemical [108,109]. Apart from the traditional techniques, researchers have also investigated alternative techniques such as ultrasonic and advanced oxidation techniques. There are many factors which influence the choice of regeneration method such as operational time and cost, consumption and regeneration efficiency [110].

In the circumstance of activated carbon, upon exhaustion or saturation with organic contaminants, it must be discarded to a landfill, incinerated, or regenerated for reuse. Even though, activated carbon is most commonly used for adsorption, there are disadvantages for this material’s use: the cost of the material and finding efficient regenerative methods [109]. In 1989, EPA estimated the regeneration cost for commercial GAC to be roughly 75% of the maintenance and operational costs [111].

3.3.1. Electrochemical Regeneration

As mentioned in earlier chapters, there is an adsorptive capacity for activated carbons when used as adsorbents, and upon exhaustion, the carbon must either be disposed or regenerated. A promising regenerative method is electrochemical regeneration which aims to restore their adsorptive capacity by electrochemically oxidising the pollutants adsorbed on the adsorbent surface. There are several mechanisms involved to achieve this outcome: one is the removal of organics by oxidation and another is direct oxidation at the adsorbent surface mirroring oxidation at a graphite electrode, both of which are aided by either electron transfer or oxidising agents. There are various parameters which affect the performance of EO and the electrochemical cell, which have been studied by numerous of researchers with the interest of the regeneration of carbon-based adsorbents [108–110].

Figure 3.6 describes in more detail, the mechanisms involved in electrochemical regeneration; with the application of an electric current across exhausted GAC, two main regeneration processes take place. Firstly, there is enhanced desorption that occurs at the surfaces of the GAC, depicted in Figure 3.6 (A) – (C), resulting with the adsorbent rid of contaminants. In Figure 3.6, (A) shows enhanced desorption due to the changes in local pH, (B) shows enhanced desorption due to changes in salinity concentration, and (C) conveys how after electro-desorption occurs, reactive species are repelled from the charged surface of GAC. Secondly, at the electrodes, electrochemical reactions and polarized GAC particles promote the degradation of the contaminants, removing them from the system entirely, as portrayed in Figure 3.6 (D). For an electrochemical regeneration process, it is ideal for both mechanisms to occur, which resultingly negates the need for further treatment [112].

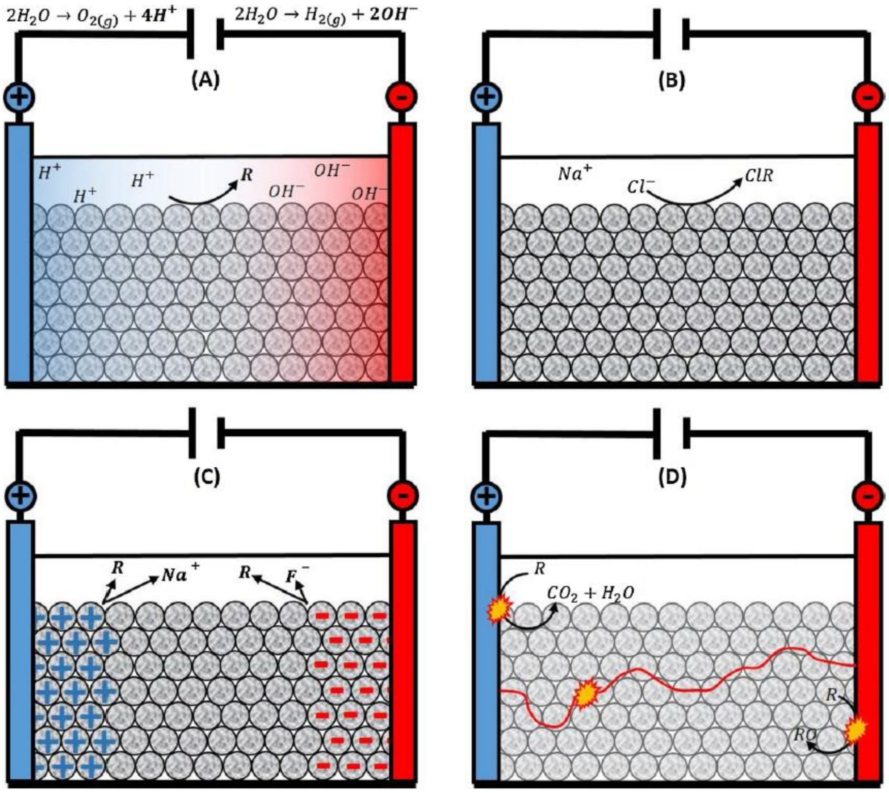


Figure 3.6: Regenerative Mechanisms Involved in the Electrochemical Regeneration of GAC [112]

There has been a wide range of publications documenting the various setups involved for regeneration with electrochemical methods such as investigating the influence of the different regions within an electrochemical cell: *Narbaitz & Cen (1994)*, and *Brown & Roberts (2007)* studied in the anodic region; whereas *Berenguer et al. (2010a)* and *Narbaitz & Karimi-Jashni, (2009)* have focussed their work in the cathodic region [12,113–115]. A range of different electrolytes have also been studies for the affect towards regeneration including NaCl *(Narbaitz & Karimi-Jashni, 2012)*, Na_2SO_4 *(Canizares et al., 2004)* and NaOH *(Berenguer et al., 2010a)* [114,116,117]. They have as well researched different reactor designs and configurations: fluidised beds and three-phase reactors *(Zhou & Lei, 2006a & 2006b)*, and fixed bed reactors *(Narbaitz & Cen, 1994)* [12,118,119]. There are several other parameters that have been studied alongside the selected in the aforementioned studies, which have yielded varied results in system performance and regeneration mechanisms.

When assessing different regeneration methods, one of the most important parameters to consider for feasibility and future applications is the regeneration efficiency. It has been stated by *Narbaitz & Cen (1994)* that to determine the regeneration efficiency, the equilibrium adsorption amount of the regenerated material is tested and compared with the equilibrium adsorption amount of the initial fresh material. The parametric relationship is shown in equation 3-9 [12].

$$\boldsymbol{Regeneration\ Efficiency}\ (\%) = \frac{\boldsymbol{Equilibrium\ adsorption\ amount\ of\ the\ regenerated\ material}}{\boldsymbol{Equilibrium\ adsorption\ amount\ of\ the\ fresh\ material}} \quad [3\text{-}9]$$

However, this equation for calculating the regeneration efficiency is somewhat flawed because if a material is not sufficiently or fully regenerated, then results are not comparable and inconsistent. *Narbaitz & Cen (1997)* have tried to explore other methods for determining regeneration efficiency; one of which is based on comparing adsorption isotherms before and after regeneration, another is conducting multiple re-loading tests with different initial concentrations hence compare loadings at equivalent liquid phase concentrations [120].

3.3.2. Electrochemical Regeneration of GAC

With focus towards the electrochemical regeneration of GAC, the first documented report was conducted by *Owen and Barry (1972)*; when compared with fresh GAC, they have managed to obtain regeneration efficiencies up to 61%. They performed their experimental procedure by placing GAC between two electrodes contained in a NaCl electrolyte. It was also reported that carbon losses were kept minimal up to 2~3% per cycle. The carbon losses per electrochemical regeneration cycle were considerably lower compared to the carbon losses obtained during thermal regeneration (5~10%). Due to the significant difference between the carbon losses of the two regeneration methods, further investigation for this method was warranted. Other advantages compared to thermal regeneration include in-situ regeneration, high regeneration efficiencies, short operational time, degradation of pollutants via oxidation at the anode, and favourably used in small- and medium-sized treatment facilities [61,121].

Since then, there have been successful attempts for electrochemical regeneration such as *Doniat et al. (1980)*, where a regeneration efficiency of 75 ~ 85% was achieved with less than 1% carbon loss per regeneration cycle [122,123]. *Narbaitz & Cen (1994)* made great advances in this field by managing to successfully electrochemically regenerate GAC that had been saturated with phenol, which is a toxic organic pollutant found in wastewater. This achievement was viewed as an accomplishment in the water treatment industry. They obtained regeneration efficiencies up to 95% by regenerating 1.2 g of GAC loaded with 128 mg of phenol by passing 100 mA of current for 5 hours. However, there was a decline of 2% in regeneration efficiency per cycle [12].

3.3.2.1. Current Density

A vital parameter of the electrochemical regeneration process is the current density, which affects both EO and energy consumption. Due to this, the current density can be viewed as a controlling parameter of the process, usually in a constant current or voltage mode depending on the type of electrochemical regeneration system [108]. *Piya-areetham et al. (2006)* concluded that increasing the current density within a given range can encourage the electrochemical degradation of organic contaminants [124]. However, a study conducted by *Wang et al. (2008b)*, demonstrated that the increase in current density had no affect towards an improved removal efficiency of COD or colour [125]. Similar findings are also observed by *Zhou & Lei (2006)*, where the change from 2 to 6 mA cm^{-2} increased the regeneration efficiency but further enhancement of the current density gave no additional improvement. Thus, suggesting it is necessary to find the appropriate balance between energy consumption and removal efficiency for electrochemical regeneration [119].

3.3.2.2. Regeneration Time

Two studies: *Xiong et al. (2003*) and *Lv et al. (2009),* have confirmed that there is a relation between the regeneration time, process performance and energy consumption. The studies proved that a greater regeneration time decreases the concentration of organic contaminants within the wastewater. Nonetheless, increasing the regeneration time was efficient up until a point; there was no significant improvement in the removal efficiency after a certain regeneration time [126,127]. *Zhang et al. (2002)* investigated the regeneration efficiency for period of 5 hours, and reported that the regeneration efficiency increased linearly with the current density from the range of 10 to 80 mA [128]. *Narbaitz & Cen (1994)* used a current range of 0 to 300 mA and a regeneration time of 2.5 hours, from which there was no improvement in regeneration efficiency higher than 100 mA. However, with increasing the regeneration time to 5 hours, the regeneration efficiency increased up to 95%. Generally, the optimal electrochemical regeneration time is defined as the time required to fulfil the wastewater discharge standards with minimum energy consumption [12].

3.3.2.3. Air Flow

The air flow rate is an unlikely parameter for electrochemical regeneration, but it does have useful purposes: one is to agitate the solution to improve the mass transfer and the other is to supply the necessary oxygen for electrochemical oxidation. In two studies: *Alvarez-Gallegos and Pletcher (1998)* and *Foller and Bombard (1995*), they studied and reported that the introduction oxygen into the system can aid the process by oxygen transforming in the oxidising agent, H_2O_2 [129,130]. This theory was challenged by *Saleh (2009)*, whose results concluded that the presence of gaseous bubbles hindered the process by disrupting the current distributions within the reactor [131].

3.3.2.4. Composition of Electrolyte

As previously mentioned, there have been studies focused on investigating how different electrolytes affect the electrochemical regeneration efficiency. It has been reported that the electrochemical regeneration of adsorbents would increase with the use of electrolytes: sodium chloride (NaCl) and sodium sulphate (Na_2SO_4). With trials using NaCl, *Narbaitz & Cen (1994)* found no significant improvement above using 1 wt. % and *Zhou & Lei (2006)* had their highest concentration of 5 g L^{-1}. In comparison of both electrolytes, NaCl yielded a higher regeneration efficiency than Na_2SO_4. There is a disadvantage for using NaCl as the electrolyte within the system, as the chlorine present may increase the toxicity of the effluent due to the possible formation of chlorinated hydrocarbons, which was the reason for *Sun et al. (2013)* to prefer the use of Na_2SO_4 rather than NaCl. [12,109,118,119]. Other electrolytes that have been studied to improve the electrochemical efficiency of adsorbents are sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) [132].

3.3.2.5. Number of Cycles

Another parameter that influences the electrochemical regeneration efficiency is the number of adsorption/regeneration cycles. *Zhou & Lei (2006)* have studied the influence of this parameter against the removal of para-nitro phenol. With a current density at 4 mA cm^{-2}, a NaCl electrolyte concentration of 5 g L^{-1} and a regeneration time of 1.5 hours, after five full adsorption/regeneration cycles, the efficiency had decreased from 89.4% to 77.7%. The reason was due to a decrease in pore volume caused by the electrochemical regeneration [118]. Another study conducted by *Sun et al. (2013)* showed a similar trend with a less significant decrease in regeneration efficiency up to 3.4%, from the first to the fifth regeneration cycle [109]. *Zhang et al. (2002)* used a current intensity of 50 mA, electrolyte concentration of 2 % NaCl and a regeneration time of 5 hours; the obtained results showed an insignificant decrease in regeneration efficiency [128].

Chapter 4

4. Nature of the Problem

With their massive contribution to civilisation, the positive applications and effects of pesticides can be outweighed by their persistence in soil and groundwater, which is combatted by remediation methods. Through the over-application and misuse of pesticides along with insufficient treatment methods, their lasting presence at low concentration levels may lead to detrimental effects towards humans, wildlife and the environment. Due to this reasons, efforts have been made into creating treatment methods that can efficiently remove pesticides from wastewater. One method that has shown promising results is adsorption, which relies on the pesticide binding to the surface of an adsorbent through physico-chemical reactions. A disadvantage associated with this process, is the saturation of the adsorbent media which slowly decreases the adsorption rate until all the active sites are used; thus, causing for the constant replacement of the adsorbent media. To tackle this drawback, regeneration methods have been employed and investigated. Limitations and low regenerative rates associated with previously used methods, has deemed electrochemical regeneration as a prospering method with achieving higher regeneration rates.

Regarding the adsorption process, the classification of the adsorption isotherms is vital and important towards the understanding and prediction of the useful parameters and characteristics of adsorption systems. Activated carbon is an extensively used adsorbent in water treatment processes due to the substance's high specific surface area caused by its porous structure. Considerably, there are various parameters which are noted to affect the adsorption efficiency and maximum adsorption capacity; parameters such as pH, temperature and surface characterisation. Regarding temperature, in most cases, elevated temperatures have shown to increase the adsorption capacity. Whereas, the influence of pH is dependent on the type of adsorbent and adsorbate used within the system. It is always notable to distinguish between the surface properties such as pore size and specific surface area, as they aid with achieving a greater adsorption rate.

Electrochemical treatment has recently become a promising water treatment method especially with wastewater contaminated with organic pollutants. Through a review of direct and indirect electrochemical oxidation of organics, it has become relevant that the reactions that take place at the surface of the electrode are different from the reactions occurring in the electrolyte solution. There is abundant literature on the electrochemical oxidation of organic pollutants; however, the literature on the application of this technique to pesticides is somewhat limited.

Unlike the vast amount of material on the electrochemical treatment of organics within wastewater, the electrochemical regeneration of adsorbents has not been widely investigated. Through literature review, it has become evident, that there are multiple parameters that can affect the regeneration efficiency of the adsorbent media, a few such as current density, electrolyte composition, time for regeneration and number of regeneration cycles. There is a proportional relation between the current density and regeneration efficiency; an increase in current density will as well increase the regeneration efficiency but only to an extent, as there is a limiting value to when current density will no longer have an effect. Various electrolyte compositions have been tested, and results have yielded NaCl as the most suited for an effective electrochemical regeneration. Similar to current density, increasing the regeneration time positively influenced the regeneration efficiency, but it should be noted that there is an optimum time limit for each system before it becomes wasteful energy consumption. On the other hand, increasing the number of adsorption/regeneration cycles, negatively affected the regeneration efficiency.

Chapter 5

5. Project Objectives

As stated in an earlier chapter, research regarding the electrochemical regeneration of adsorbents is limited when compared with other regenerative methods. Therefore, this project was initiated as a response to the lack of research into electrochemical regeneration of GAC saturated with micropollutants: pesticides, with the interest of exploring operational conditions which yielded sufficient regenerations along with low cost and environmental footprint. The main objectives are analysing and assessing the feasibility and efficiency of the water treatment method, adsorption combined with electrochemical regeneration. The treatment methods investigated in this project are focused on waters specifically contaminated with pesticides; Thus, providing the overall objective and problem question of this thesis:

"How is the removal of pesticides, represented by RNO, affected by the alteration of adsorption's operational parameters and is in-situ electrochemical regeneration a feasible and suitable regenerative method for exhausted GAC?"

5.1. Project Strategy

In order to fulfil this overall object and problem statement, the following specific research tasks and questions are addressed:

- Study the kinetics of the adsorption treatment process. How is the adsorption process affected with the alteration of different operational parameters?
- How is the adsorption capacity of a system affected with the differing in adsorbent amounts? How does the calculated adsorption capacity vary from the experimentally sourced adsorption capacity?
- Investigate the adsorption isotherm model the adsorption system follows, and what does the results imply?
- What is the rate order model the adsorption kinetics of the system follows?

- Investigate the efficiency of regeneration and the influence of optimising various parameters have towards the process. How are they affected?
- If classed as a suitable regenerative method, can it be applied to large scale applications?

To answer the questions and gain a greater insight into this topic, an experimental plan was conducted. With regards to this project, the experimental section is separated into two section phases: firstly, investigating the adsorption capacity of the GAC and removal of the target dye contaminant (phase I), followed by the electrochemical regeneration process (phase II) as shown in Figure 5.1.

Concerning the adsorption experimental work, experimental focus was steered towards the adsorption kinetics, isotherm studies and the influence of adsorption parameters such as temperature, and adsorption combined with electrochemistry. The experimental kinetic data was analysed using both pseudo-first order and pseudo-second order rate models. With the use of the Freundlich, Temkin and Langmuir isotherm models, it was possible to analyse the isotherm data of the applied adsorption system. A developed electrochemical batch reactor was used for a portion of the adsorption experiments and was planned to be used for the electrochemical regeneration of RNO saturated HGR-activated carbon (HGR-AC). The regeneration parameters such as regeneration time, current intensity, and number of regeneration cycles have been studied through in-detailed literature review of previously conducted studies.

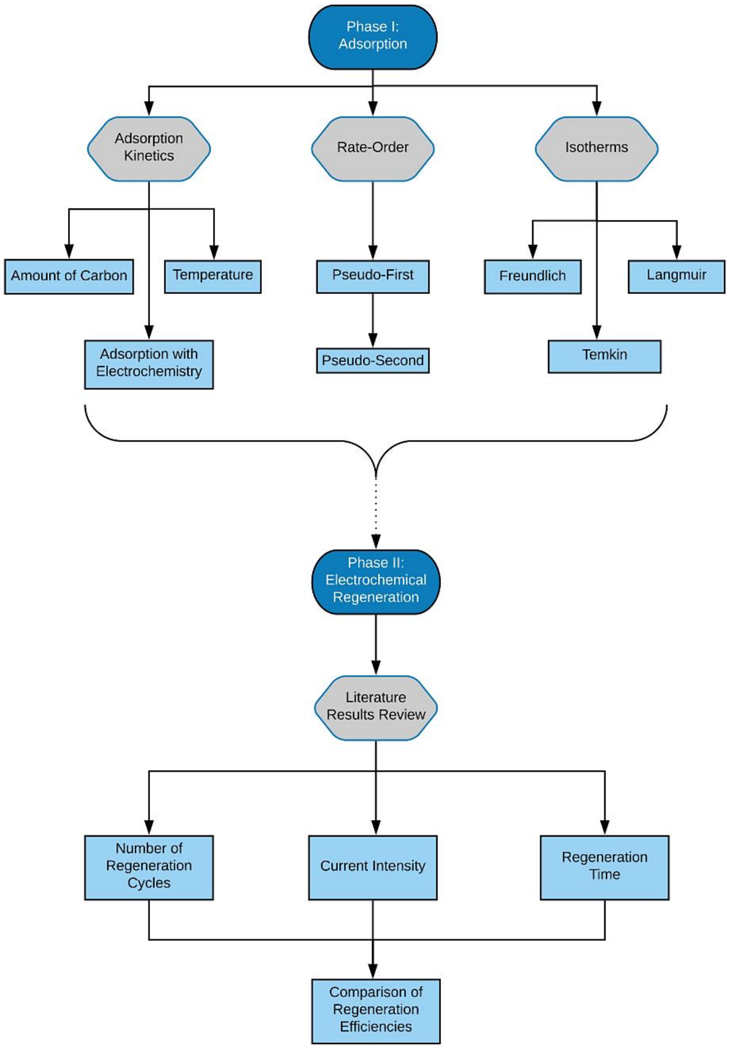


Figure 5.1: Experimental Layout Flowchart

Chapter 6

6. Materials and Methods

6.1. Materials

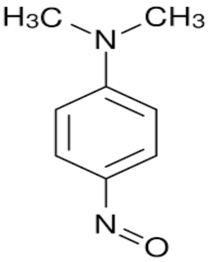
6.1.1. Adsorbent

The sole adsorbent used in this project is HGR-AC supplied by Silhorko-Eurowater A/S, Hillerød. HGR-AC is a sulfur impregnated carbon material. This type of activated carbon possesses a unique pore structure and superior hardness, as a result to the base carbon being comprised of selected bituminous coal and binders [133].

6.1.2. Adsorbate

RNO, also known as "*4-Nitroso-N,N-dimethlyaniline*" was utilised as the target dye contaminant in this project. The dye is classed as commercial grade and was supplied by Sigma-Aldrich Chemie GmbH; regarding experiments, the dye was used without further purification. The RNO dye solutions were prepared using demineralised water and had to be continuously mixed overnight to allow ample enough time for the powder to fully dissolve. The chemical structure and the characteristics of RNO are shown in Table 6.1.

Table 6.1: Physico-chemical Characteristics of RNO

Technical Name	4-Nitroso-N,N-dimethlyaniline
Common Name	RNO
Molecular Formula	$C_8H_{10}N_2O$
Molecular Weight [g M^{-1}]	150.18
Purity [%]	≥95.0
λ_{max} [nm]	440
pKa	4.544
Log(K_{OW})	2.04
Log(K_{OC})	1.85
Molecular Structure	

λ_{max}: wavelength of maximum absorbance; pKa: acid dissociation constant

The RNO dye solution concentration was determined using a Cary 60 UV-Vis spectrophotometer by Agilent Technologies. The samples were placed in spectrophotometer disposable cuvettes with a 10 mm light pathlength. Through research, the wavelength for maximum absorbance was established to be at 440 nm [134].

For the calibration method, 25 mg of 4-Nitroso-N,N-dimethlyaniline was measured and placed in a 1 L volumetric flask and made up to the mark using demineralised water . Thus, making the concentration of RNO to 25 mg L^{-1}. From the 1 L volumetric flask, dilutions were made to have standard solutions with concentrations ranging between 0.50 to 25 mg L^{-1}. The absorbances of these standard solutions were measured and plotted against concentrations. The Beer-Lambert law was used for this process and yielded the $A = 0.176419C$

6.1.3. Electrodes: Steel-316 and DSA

For water treatment, there is an array of electrodes that can be used for electrolytic treatments. Each type of metallic material possesses unique chemical properties, all of which can influence towards the adsorption and electrochemical regeneration. For this project, steel-316 was selected as the cathode and a DSA for the anode, due to economic consideration and availability.

The DSA (dimensionally stable anode) used was a titanium plate covered with mixed-metal oxides that has been optimised for oxygen production. DSAs have proven to be good conductors with high catalytic activity along with long operating life. The choice of titanium for the anode plate material is because titanium is a cheaper material option, when compared with other materials such as silver and platinum. Another advantage for using a titanium DSA is that there is no contamination to the water quality by the degradation of the plate due to the low concentrations of ions from the mixed-metal coating [135].

The cathode selected was stainless steel type 316 (SS-316). Due to their longevity, steel is usually the least expensive option considered. This is a result of their alloy compositions that include chromium and nickel, which gives the material corrosion-resistant properties. Another advantage for using this type of stainless steel, is that it does not require additional chemical additives to the environment to preserve the material from corrosion [136] [137].

6.1.4. Batch Reactor

For the experiments that involved the application of electric potential, they were conducted in a developed man-made electrochemical “reactor”. This reactor was purposed for batch trials, and the apparatus includes a sieve pouch which is connected to a lid with two attached electrodes: DSA as the anode and SS-316 electrode as the cathode, as aforementioned. The electrodes are connected to a power bank where the DC voltage and DC current can be altered. The lid can then be placed on a beaker which completes the reactor design as shown in Figure 6.1.

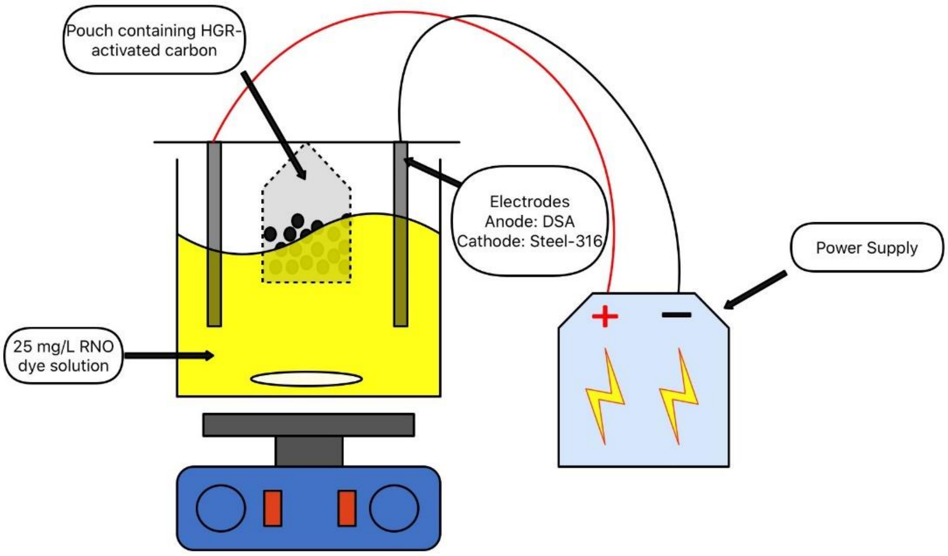


Figure 6.1: Electrochemical Reactor Design Set-up

Regarding the electrodes in the batch reactor, only certain sections were submerged in the adsorbate; the sizing specifications and effective surface areas are shown in Table 6.2.

Table 6.2: Electrode Sizing Specifications

Electrode Material		Size [cm]	Effective Surface Area [cm^2]
Anode	DSA	9.5 x 4.5 x 0.2	64.2
Cathode	Stainless Steel 316	9.5 x 4.5 x 0.2	34.95

6.2. Methods

6.2.1. Analytical Methods

6.2.1.1. UV-Vis Spectroscopy

The UV-Vis spectrophotometer used to analyse all the samples for this project is the Cary 60 UV-Vis spectrophotometer provided by Agilent Technologies. UV-Vis spectrophotometry is a quantitative analytical tool which entails the absorption of near-ultraviolet or visible radiation, in the given wavelength range between 200 nm and 780 nm, passed through different analytes. The functionality of a UV-Vis spectrophotometer generally depends on a beam of UV-light and an electronic detector [138].

This analytical method is used to determine the concentration of the absorbate solution that contains transition metallic ions and highly conjugated organic compounds. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species within the solution and path length. This means, that with an established fixed path length, this tool can be utilised for both concentration determination and the absorbance changes regarding differing concentrations, which are determined from a calibration curve [139].

The Beer-Lambert law, which was used to describe the relationship between concentration and absorbance as displayed in equation 6-1:

$$\boldsymbol{A = \varepsilon\, l\, C} \qquad [6\text{-}1]$$

Where,

A represents the absorbance

ε is the molar absorptivity (L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$)

l is the pathlength through the sample (mm)

C is the concentration of the sample (mg $\mathrm{L^{-1}}$)

6.2.2. Kinetics/Equilibrium Studies

To investigate the adsorption kinetics for this project, batch experiments were conducted using varied amounts of HGR-AC, ranging between 10 mg to 500 mg. The batch experiments were carried out in beakers which contained 250 mL of 25 mg $\mathrm{L^{-1}}$ concentrated RNO dye solution, that was constantly magnetically stirred at 900 revs/min; samples were extracted using disposable 3 mL pipettes at regular time intervals over four hours and analysed using UV-Vis spectroscopy. As prior mentioned, the influence of applied electric potential and temperature were also investigated. Following the prior instilled four-hour experimental run time period, the analysis used to determine the influence of temperature was carried out by elevating the temperature of the analyte to 75 °C at specific time periods of the experimental run. Those chosen time periods are: the beginning of the experiment; at the point of equilibrium; and after equilibrium had been reached. For the combined adsorption and applied electric potential investigation, the adsorption process was carried out with the application of operating voltages ranging between 1 V and 15 V. In the entirety of the project, all samples have been conducted and analysed in triplicates at each selected time period, and the obtained mean values were used for further calculations when necessary for this project.

Due to the nature of the experimental plan, the initial adsorption kinetic experiments are separated into different batches to investigate the influence of the amount of HGR-AC added to the system. Samples were extracted and analysed accordingly at regular time intervals. Table 6.3 shows the overview of which HGR-AC content is associated to which batch.

Table 6.3: Initial Experimental Plan for Adsorption Kinetics

Batches		**Added Carbon Content [mg]**
Label	**Trials**	
1	1.1	10
	1.2	
	1.3	
2	2.1	50
	2.2	
	2.3	
3	3.1	100
	3.2	
	3.3	
4	4.1	250
	4.2	
	4.3	
5	5.1	500
	5.2	
	5.3	

After fully completing the initial experimental trials and assessing the mean values for each batch. A single batch was then selected as the main experimental batch for future selections. As an affecting parameter towards the adsorption process, the effect of temperature towards the adsorption rate was investigated. The next experimental plan for this project is shown in Table 6.4; the intention was to study how significantly temperature affected the adsorption rate and kinetics. Thus, prompted changing the times at which temperature was applied to the adsorption system: such as at the beginning of the experiment (0 minutes), the time at which equilibrium was reached in the prior experiments (120 minutes), and after equilibrium was reached (210 miuntes).

Table 6.4: Experimental Plan for the Investigation of the Influence of Temperature

Batches		Added Carbon Content [mg]	Time of Applied Temperature [mins]	Temperature Applied [°C]
Label	**Trials**			
T1	T1.1	100	0	75
	T1.2			
	T1.3			
T2	T2.1	100	120	75
	T2.2			
	T2.3			
T3	T3.1	100	210	75
	T3.2			
	T3.3			

For the influence of temperature experimental investigation, batch tests were made in a similar manner compared to the prior experimental layout. They were made in 600 mL beakers containing 250 mL of 25 mg L^{-1} concentrated RNO dye and 100 mg of HGR-AC and was constantly magnetically stirred. The batches were then heated to 75 °C at their designated times displayed in Table 6.4, and were constantly monitored to counteract any temperature fluctuations that may have occurred. Samples were extracted and analysed accordingly at regular time intervals.

To investigate the combined relationship between adsorption and applied electric potential, the experimental layout shown in Table 6.5 was conducted. As portrayed in the table, the adsorption experimental trials were carried out with a fixed applied current of 200/300 mA and different operating voltages ranging between 1V and 15V. Comparable to previous conducted experimental setups, the batch experiments were carried out in a developed reactor and were constantly magnetically stirred. For each batch trial, the allocated operating voltage was applied from the beginning of the experiments and throughout. Initially, background tests were performed without HGR-AC to see solely the affect of applied electric potential had towards the system.

Table 6.5: Experimental Investigation of the Combined Relationship of Adsorption and Electrochemistry

Batches		Added Carbon Content [mg]	Applied Voltage [V]
Label	**Trials**		
E1	E1.1	100	1
	E1.2		
	E1.3		
E2	E2.1	100	2.5
	E2.2		
	E2.3		
E3	E3.1	100	5
	E3.2		
	E3.3		
E4	E4.1	100	10
	E4.2		
	E4.3		
E5	E5.1	100	15
	E5.2		
	E5.3		

6.2.3. Adsorption Isotherms

The isotherm constants have been determined by linearising the original forms of the isotherms and using the correlation coefficient, r^2, to evaluate the which isotherm is most fitting. The linear regressions for each adsorption isotherm was performed using Microsoft Excel, and the correlation coefficient can be used as a distinguishing comparison factor between the different isotherm models. Through linearisation and graphical plots: the linear Langmuir model is obtained by plotting $\frac{1}{q_e}$ against $\frac{1}{C_e}$, the linear Freundlich model is from a plot of log (q_e) vs. log (C_e), and the Temkin model in linear form is achieved by plotting q_e against lnC_e.

Also involved with the determination of the adsorption isotherms, the obtained data from the experimental kinetic studies was utilised to acquire the adsorption capacity of the system. The adsorption capacity at equilibrium was calculated through a mass balance equation across the liquid and solid phases, as shown in equation 6-9:

$$\boldsymbol{q_e} = \frac{(\boldsymbol{C_0}-\boldsymbol{C_e})\boldsymbol{V}}{\boldsymbol{m}} \qquad [6\text{-}9]$$

Where,

q_e represents the amount of adsorbate loaded onto the adsorbent at equilibrium (mg g^{-1})

m is the dry weight of the adsorbent added to the system (g)

C_0 is the initial concentration (mg L^{-1})

C_e is the concentration at equilibrium (mg L^{-1})

V is the volume of the dye solution (L)

6.2.4. Electrochemical Regeneration

The electrochemical regeneration of activated carbon was investigated through the evaluation of various results: in the form of regeneration efficiencies; obtained from multiple published studies that were previously mentioned in the literature review in chapter 3.3.2. Similar to the adsorption experimental investigation, the electrochemical regeneration will be investigated through the variation of different operational parameters such as regeneration time, current intensity and the number of regeneration cycles.

For the investigation of each operational parameter, a total of three studies were selected from the literature review, as shown in Table 6.6, Table 6.7 and Table 6.8. The results concerning the chosen parameter, was then taken from each study and compared with one another to have an overview at how the parameter's affected the regeneration efficiency. After which, all the regeneration efficiencies will be grouped and compared as a whole.

Table 6.6: Electrochemical Regeneration - Regeneration Time Studies

Regeneration Time Studies		
Study Name	Operating Conditions	Regeneration Time [hrs]
Zhang (2002)	2% NaCl	8
Narbaitz & Cen (1994)	1% NaCl, 10 mA	10
Zhou & Lei (2006)	5 g L^{-1} NaCl, pH 3, 4 mA cm^{-2}	2

Table 6.7: Electrochemical Regeneration - Regeneration Cycle Studies

Regeneration Cycle Studies		
Study Name	Operating Conditions	Number of Regeneration Cycles
Zhang (2002)	2% NaCl, 50 mA, 5 hour regeneration time	4
Sun et al. (2013)	1 g L^{-1} Na_2SO_4, 2 A	5
Zhou & Lei (2006)	5 g L^{-1} NaCl, pH 3, 4 mA cm^{-2}	5

Table 6.8: Electrochemical Regeneration - Regeneration Current Intensity Studies

Regeneration Current Intensity Studies		
Study Name	Operating Conditions	Current Intensity [mA & A]
Sun et al. (2013)	1 g L^{-1} Na_2SO_4	1 A
		2 A
		3 A
Zhang (2002)	2% NaCl, 5 hour regeneration time	15 mA
		30 mA
		50 mA
		80 mA
Narbaitz & Cen (1994)	1% NaCl	10 mA
		30 mA
		50 mA
		100 mA

Since it is not possible to obtain all the experimental data from the previously stated studies, a portion of the results have been made in estimation to give a portrayal of how the regeneration efficiency reacts to the different operational conditions. These models and results were made using Microsoft Excel. The results collected directly from the studies have been stated as normal, whereas the excel-estimated results are denoted with a '~' sign before the result. This is to represent that the presented value is an estimation within a 2-3% error-range of the experimentally obtained value.

Chapter 7

7. Results and Discussion

7.1. Phase I: Adsorption

7.1.1. Adsorption Kinetics/Equilibrium Studies

The investigation regarding the adsorption kinetics and equilibrium studies for RNO onto HGR-AC were firstly conducted at room temperature, in a batch system setup, where the only variable was the amount of HGR-AC added to the adsorption system. Five systems were created and carried out where the amount of adsorbent ranged from 10 to 500 mg. The mean concentration levels of the adsorption system at the specified run-times are shown in Figure 7.1, along with the final mean concentrations of the batches at the end of the experimental trials in

Table 7.1. The mean results from this section have been considered with the standard deviations of the original data ranging between ±3~7.5. As shown in the figure, the adsorption of RNO immediately takes place at a rapid rate, causing the dye concentration to decrease within the first 5 minutes for all the batches. The fast decrease in RNO concentration is explained by the high driving force of the initial mass transfer of the dye onto the external surface of the adsorbent.

It is noticeable that batch 1 with 10 mg of added HGR-AC plateaus approximately at a concentration of 14 mg L^{-1}, five minutes after the experiment had begun. Moreover, for three of the batches: 100, 250, and 500 mg, there is a similar trend that is observed: over time, the concentration of RNO decreases uniformly until equilibrium is reached and then levels out. However, batch 2 which contained 50 mg of HGR-AC had an abnormal trend, as displayed, this batch did not have an initial adsorption rate compared to the other batches. After 30 minutes, batch 2 surpassed the adsorption concentration of batch 1 before the concentration began to gradually decrease until equilibrium was reached. Figure 7.1 shows that equilibrium was achieved after approximately 120 minutes for all batches except batch 1, despite there being a gradual decrease in the RNO concentration that continued as time increased. In

Table 7.1, with the support of Figure 7.1, a trend is visible, increasing the added HGR-AC amount to the adsorption system, will result in the decrease of the final concentration. There is also an increase in removal efficiency and amount of RNO adsorbed during the process.

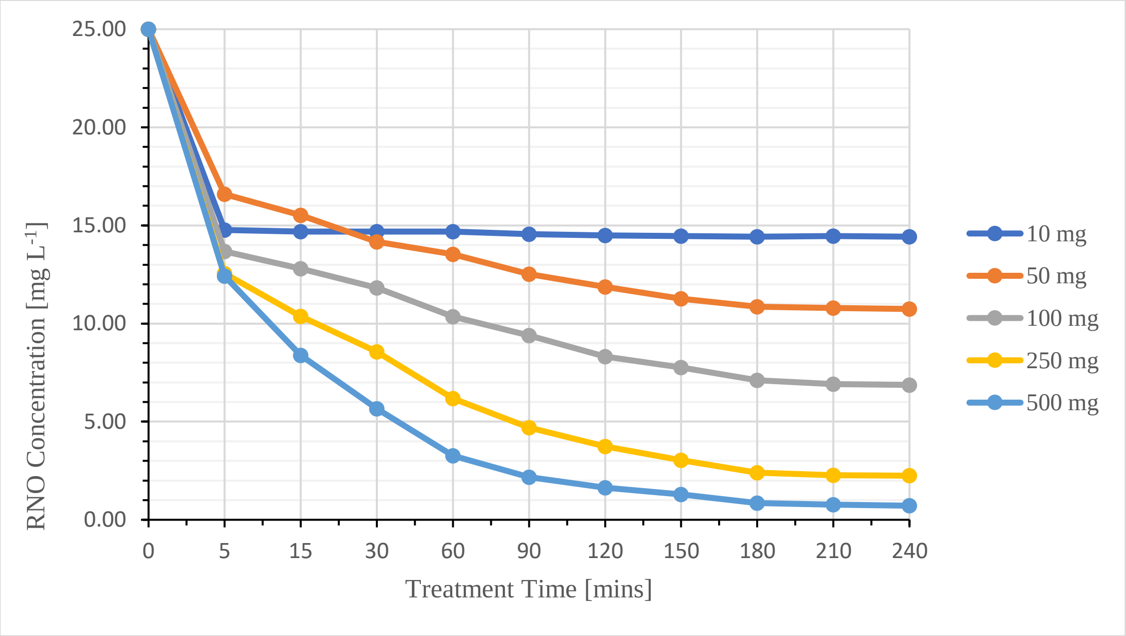


Figure 7.1: The adsorption rate of RNO onto Different Amounts of HGR-AC (10 mg - 500 mg)

Table 7.1: Final Mean Concentrations from Initial Adsorption Kinetic Trials

Batch Label	Final RNO Concentration [mg L^{-1}]	RNO Adsorbed [mg g^{-1}]	Removal Efficiency [%]
1 (10 mg)	14.43	10.57	42
2 (50 mg)	10.74	14.26	57
3 (100 mg)	6.87	18.13	72
4 (250 mg)	2.25	22.75	91
5 (500 mg)	0.72	24.28	97

In Figure 7.2, the experimental data regarding adsorption and the influence of temperature is shown. From the graph, it can be viewed that the temperature of 75 °C has no significant influence towards the system until after 180 minutes, where it surpasses the concentration of the initial adsorption experiment that was conducted at room temperature. The figure does suggest that temperature has some effect on the adsorption process, when temperature is applied from the beginning of the experiment. The final mean concentrations and removal efficiencies for the adsorption batches are shown in Table 7.2, and it states batch T1 is the only batch which successfully reached a lower concentration than the original adsorption experiment (batch 3 in Table 7.1). T2 and T3, where temperature was applied at 120 and 210 minutes, respectively; achieved a lower degradation rate and did not reach low concentration levels. Regarding the original adsorption experiments from Figure 7.1, equilibrium was reached at approximately 120 minutes. However, for the temperature experiments at the same time period of 120 minutes, adsorption continues to take place with a noticeable decrease in concentration. There is no indication of the adsorption rate decreasing; thus, making it not possible to reach equilibrium within the experimental runtime.

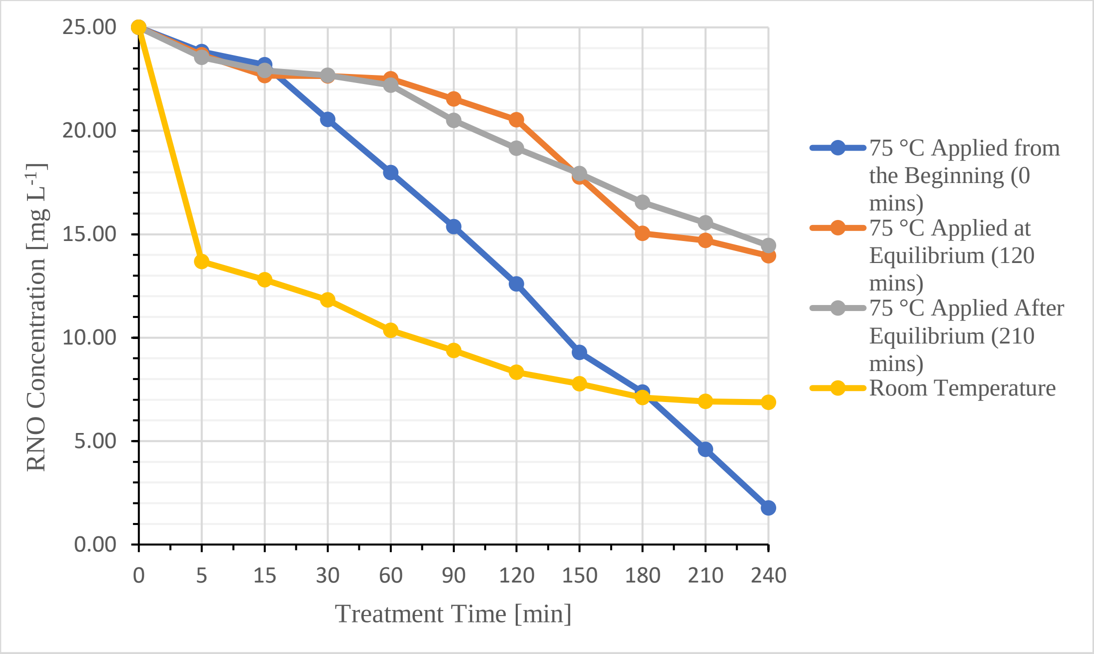


Figure 7.2: The Adsorption Rate of RNO onto 100 mg HGR-AC with the Influence of Temperature

Table 7.2: Final Mean Concentrations from Adsorption Kinetic Trials with the Influence of Temperature

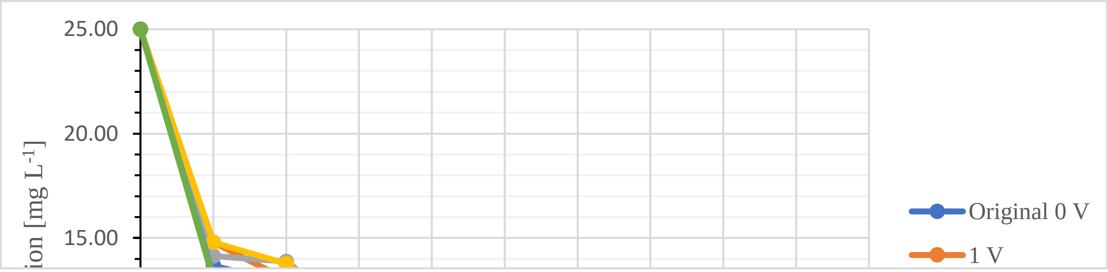
Batch Label	Final RNO Concentration [mg L^{-1}]	RNO Adsorbed [mg g^{-1}]	Removal Efficiency [%]
T1 (0 mins)	1.77	23.23	93
T2 (120 mins)	13.95	11.05	44
T3 (210 mins)	14.45	10.55	42
Original (100 mg – Room Temperature)	6.87	18.13	73

The results from the experimental investigation of adsorption combined with applied electric potential are presented in Figure 7.3 and Table 7.3. It was also of interest to see the effects of EO towards dye degradation, and they are presented in Appendix II through Figure 10.2 and Table 10.1. From the graph in Figure 7.3, there is uniform degradation for all the batches. Applied electric potential proved to have a positive influence towards the adsorption process and the degradation of the dye; all the batches yielded a final concentration lower than the standard batch, which ran without any electrochemical aid. A trend can be viewed, showing the increase in applied electric potential further increases the degradation process to achieve lower dye concentrations. However, for the batches E1 and E2, which used 1 and 2.5 V, respectively, during the first 30 minutes of the experimental run, the batches had a lower removal rate than the original experiment. Another observation is that throughout the experimental run, the two batches had similar concentrations as the original experiment on multiple occasions, which suggested that 1 and 2.5 V does not significantly affect the adsorption process. In Table 7.3, batches E1 and E2 were unable to decrease the final dye concentration further than 1 mg L^{-1} from the original experiment, which further emphasised that the operating voltage was not at a high enough value to show significant aid towards the degradation process. Whereas, batches E3, E4 and E5 using 5, 10 and 15 V, respectively, obtained greater dye degradations during the experiments to achieve lower final mean concentrations of 5.24, 4.27 and 3.02 mg L^{-1}, respectively. Additionally, batch E5, which used the highest operating voltage, showed to gain a final concentration that was less than half of the original run. These findings support the theory that increasing the established operating voltage will sequentially increase the removal rate and efficiency; moreover, decrease the final mean concentration. Another noticeable fact from Figure 7.3, is that adsorption equilibrium was not reached within the experimental time.

Table 7.3: Final Mean Concentrations from Adsorption Kinetic Trials with the Influence of Electrochemistry

Batch Label	Final RNO Concentration [mg L^{-1}]	RNO Adsorbed [mg g^{-1}]	Removal Efficiency [%]
E1 (1 V)	6.22	18.78	75
E2 (2.5 V)	5.91	19.09	76
E3 (5 V)	5.24	19.76	79
E4 (10 V)	4.27	20.73	83
E5 (15 V)	3.02	21.98	88
Original (100 mg – 0 V)	6.87	18.13	73

The RNO removal efficiencies and dye removal amounts for all the reported experiments are displayed in Figure 7.4 and Table 7.4. From both the table and figure, it can be seen most experiments gain an increase in removal efficiency from the original (100 mg) experiment: all the adsorption combined with applied electric potential and one of the temperature experiments. The original adsorption experiment with 100 mg of HGR-AC yielded an RNO removal efficiency of 73% and adsorbed 18.13 mg L^{-1}. Moreover, as stated earlier, only one



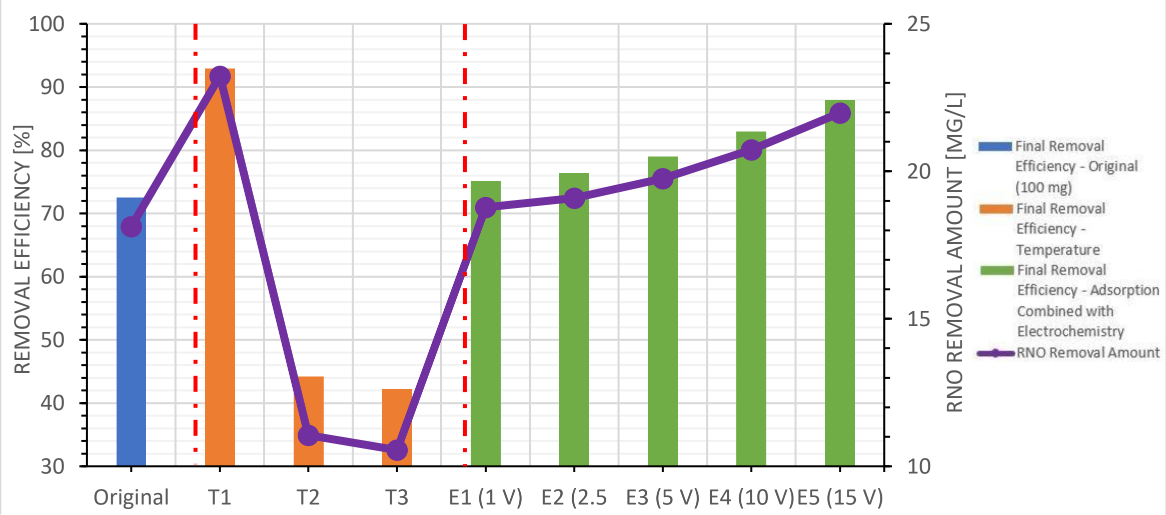


Figure 7.4: Removal Efficiencies and Adsorbed Amounts for All Adsorption Kinetic Trials

of the temperature experiments, T1, showed to degrade the RNO dye further than the original; and from the table, this enhanced degradation resulted in the removal efficiency to increase by 20%. Additionally, all the experiments that consisted of adsorption combined with applied electric potential proved that the removal efficiency also follows the trend, in which increasing the applied voltage positively influences the removal efficiency and dye removal. The maximum obtained removal efficiency was 88% with 21.98 mg L^{-1} of RNO removed.

Table 7.4: Final Mean Concentrations and Removal Efficiencies for All Adsorption Kinetic Trials

Batch Label	RNO Removal Amount [mg L^{-1}]	Final Removal Efficiency [%]
Original (100 mg)	18.13	73
T1 (75 °C at 0 mins)	23.23	93
T2 (75 °C at 120 mins)	11.05	44
T3 (75 °C at 210 mins)	10.55	42
E1 (1 V)	18.78	75
E2 (2.5 V)	19.09	76
E3 (5 V)	19.76	79
E4 (10 V)	20.73	83
E5 (15 V)	21.98	88

7.1.2. Rate Order Determination

With relation to equation 3-10, plotting $\log(q_e - q_t)$ against t should give a linear relationship, to which the values of k_1 and r^2 can be obtained; the obtained plot and values are displayed in Appendix III through Figure 10.3 and Table 10.2. Due to batch 1 not accordingly following a pseudo-first order model, all the batches were tested against a pseudo-second order model. Regarding equation 3-13, the linear relationship to obtain k_2 and r^2 is achieved by plotting $\frac{t}{q_t}$ against t as portrayed in Figure 7.5. The figure showed that the slope increased with the decrease of adsorbent added to the system which is also supported by Table 7.5. The correlation coefficients for all batches were significantly higher than the correlation coefficients for the pseudo-first order model, which indicated that the pseudo-second order model is a good fit for all the batches.

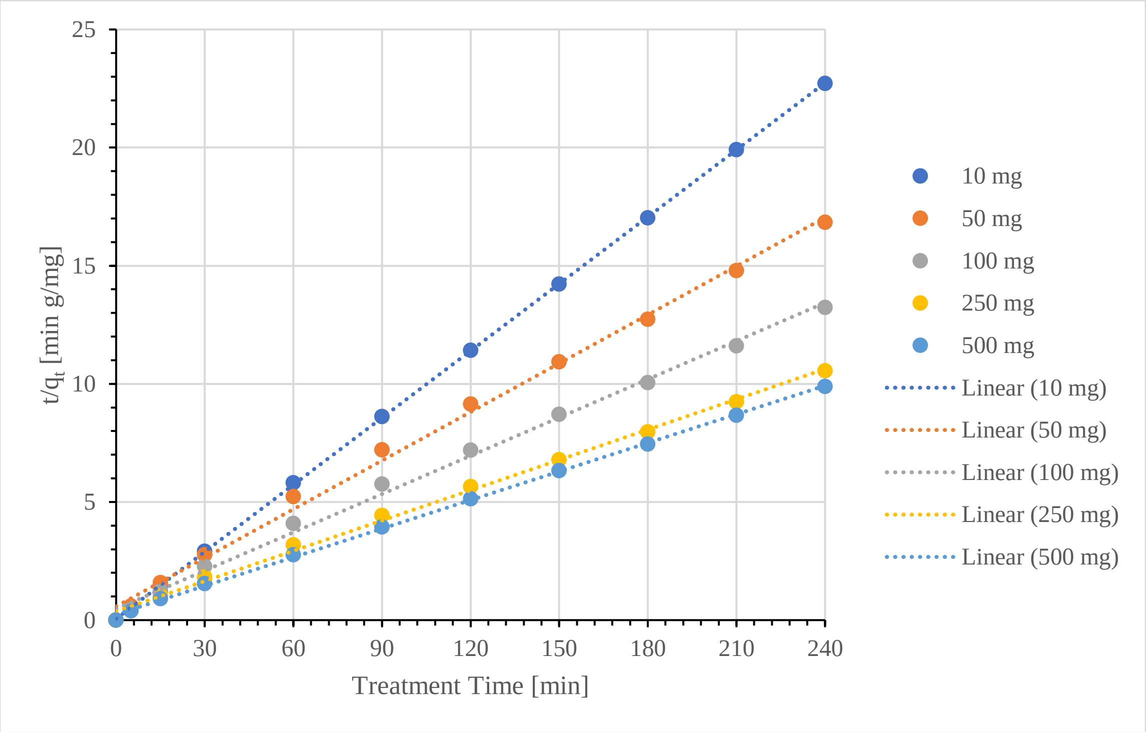


Figure 7.5: Pseudo-Second Order Adsorption Kinetics of RNO onto Different Amounts of HGR-AC (10 mg – 500 mg)

Table 7.5: Kinetics Parameters for Adsorption of RNO using Pseudo-Second Order Linear Equations

Carbon Amount [mg]	$q_{e,\,exp}$ [mg g^{-1}]	k_2 [min^{-1}]	r^2
10	10.2267	0.0945	0.9997
50	13.1300	0.0686	0.9966
100	16.6767	0.0540	0.9960
250	21.2600	0.0428	0.9973
500	23.3733	0.0403	0.9992

$Q_{e,\,exp}$: experimentally calculated amounts of adsoprtion at equilibrium; k_2: pseudo-first order rate constant; r^2: correlation coefficient

7.1.3. Adsorption Isotherms

The linear regressions and their r^2 values of the Langmuir, Freundlich and Temkin adsorption isotherm models are shown in Figure 7.6, Figure 7.7 and Figure 7.8, respectively. By comparison of the correlation coefficients of the experimental data regarding the isotherm models, the Temkin model gave the best correlation with the highest r^2 value of 0.9283; followed by the Freundlich model as the second-best fitting model. The Langmuir model showed a bad correlation with a low value of 0.5713. The results suggest that adsorption mechanisms for this system follow a Temkin model.

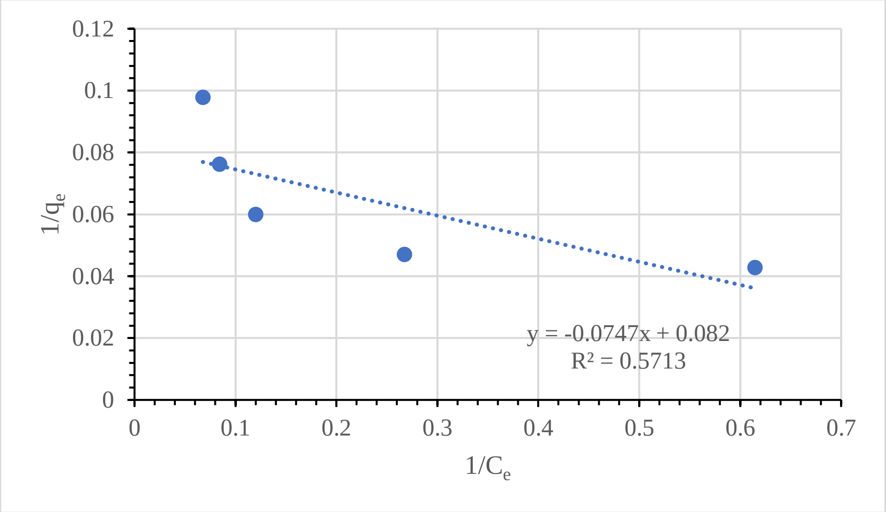


Figure 7.6: Linear Langmuir Adsorption Isotherm Model for RNO onto HGR-AC

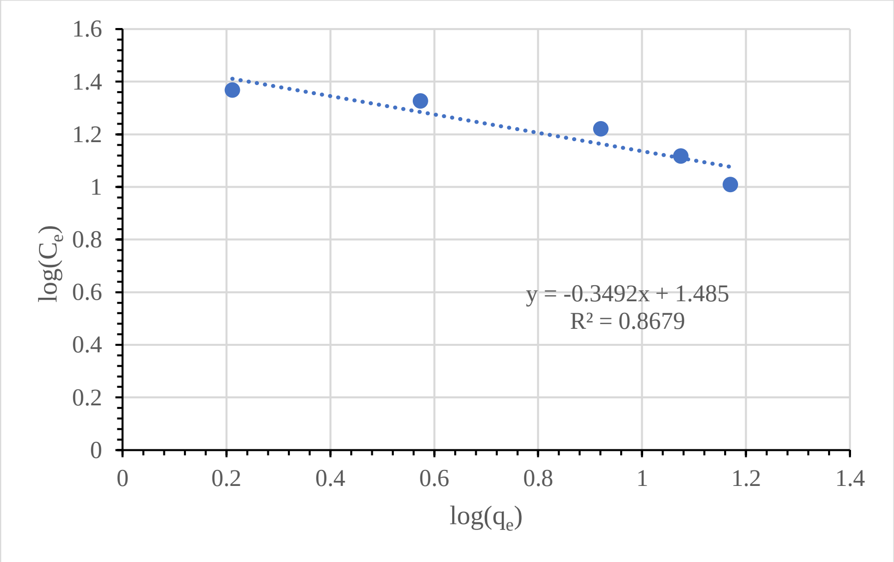


Figure 7.7: Linear Freundlich Adsorption Isotherm Model for RNO onto HGR-AC

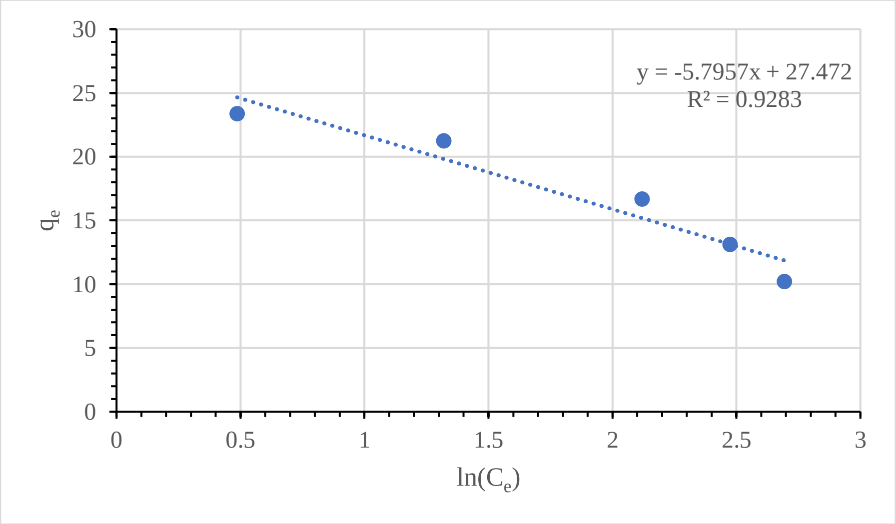


Figure 7.8: Linear Temkin Adsorption Isotherm Model for RNO onto HGR-AC

The equilibrium adsorption amounts for the initial adsorption batch trials are displayed in Table 7.6. From the table, there is a clear significant difference between the equilibrium adsorption amounts between the calculated and the experimentally obtained. All the batches except batch 4 shown a difference in equilibrium adsorption amounts. For the calculated equilibrium values, the adsorption amount decreases with the increase in added HGR-AC amount; which is the opposite for the experimentally obtained values. To explain the calculated equilibrium values, the decrease in adsorption amount is due to the adsorptive capacity of the adsorbent not being fully utilised at higher adsorbent dosages, when compared with lower. The increase in adsorbent dose could cause aggregation of the adsorbent, which therefore affects the decreases the adsorption capacity with the increase in adsorbent dose.

Table 7.6: Equilibrium Adsorption Amounts of Different HGR-AC added to 25 mg^{-1} RNO Dye

Batch	Carbon Amount [mg]	$q_{e,\,exp}$ [mg g^{-1}]	$q_{e,\,cal}$ [mg g^{-1}]
1	10	10.2267	255.668
2	50	13.1300	65.650
3	100	16.6767	41.692
4	250	21.2600	21.260
5	500	23.3733	11.687

$q_{e,\,exp}$ and $q_{e,\,cal}$; experimental and calculated amounts of adsorption at equilibrium

7.2. Phase II: Electrochemical Regeneration

As mentioned previously, part of the results are denoted with '~' to show the value was obtained from a published graph, then visually copied and plotted in Microsoft Excel; to be within a given error-range of 2-3%. The results from the regeneration time trials, consisting of data from *Zhang (2002)*, *Narbaitz & Cen (1994)* and *Zhou & Lei (2006)* are displayed in Figure 7.9 and

Table 7.7. From the figure, it is evident that the regeneration efficiency increases with the increase in regeneration time allocated for a cycle; as all three studies yielded positive results for this theory. *Zhou & Lei (2006)* managed to obtain 92% regeneration in the span of two hours; whereas, *Narbaitz & Cen (1994)* and *Zhang (2002)* who used a longer allocated regeneration time obtained ~87% and ~79%, respectively. Another noticeable observation was that, for each of the systems, there was a time-limiting value that was reached before the regeneration efficiency plateaued; *Zhou & Lei (2006)* and *Zhang (2002)* seemed to

experience this. The highest regeneration efficiency of 95% is not shown in the Figure 7.9, but in

Table 7.7 and was achieved after 40 hours by *Narbaitz & Cen (1994)*.

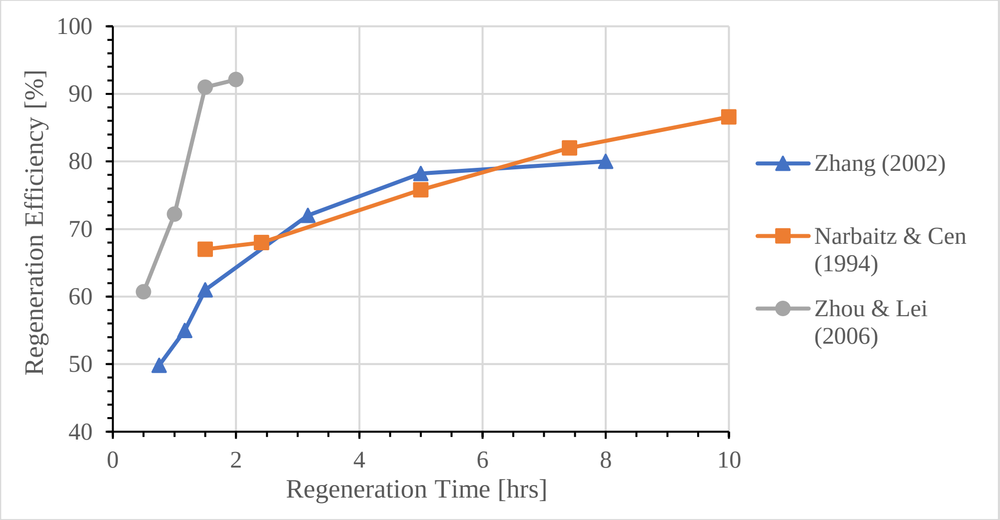


Figure 7.9: Change in Regeneration Efficiency with respect to Regeneration Time

Table 7.7: Final Regeneration Efficiency for Regeneration Time Studies

Regeneration Time Results		
Study Name	Regeneration Time [hrs]	Final Regeneration Efficiency [%]
Zhang (2002)	8	~79
Narbaitz & Cen (1994)	10 & 40	~87 & 95
Zhou & Lei (2006)	2	92

The results regarding the influence of regeneration cycles towards the electrochemical regeneration efficiency is shown in Figure 7.10 and

Table 7.8. From the figure, the regeneration efficiency is negatively affected with the increase in the number of regeneration cycles. All studies showed a clear decrease in regeneration efficiency, two of the studies: *Sun et al. (2013)* and *Zhang (2002)* showed a loss less than 5% in efficiency to obtain the final regeneration efficiencies of 91% and ~70%. Meanwhile, *Zhou & Lei (2006)* decreased over 10% in regeneration efficiency from its first cycle: 89% to 78%.

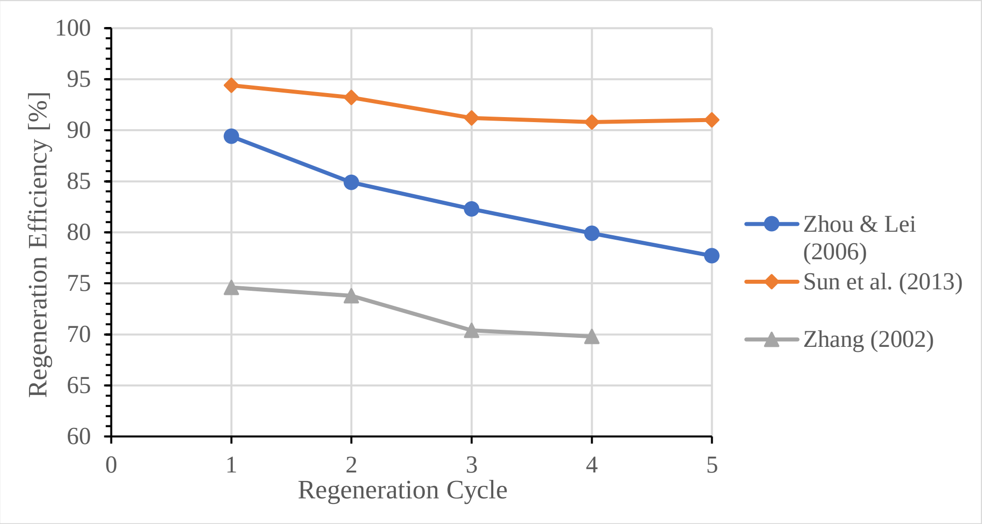


Figure 7.10: Change in Regeneration Efficiency with respect to Regeneration Cycles

Table 7.8: Final Regeneration Efficiency for Regeneration Cycle Studies

Regeneration Cycle Studies		
Study Name	Number of Regeneration Cycles	Final Regeneration Efficiency [%]
Zhang (2002)	4	~70
Sun et al. (2013)	5	91
Zhou & Lei (2006)	5	78

Due to the large amount of results from the conducted studies regarding the influence of current intensity towards the electrochemical regeneration efficiency, the results are separated and displayed in Figure 7.12, Figure 7.11 and Table 7.9. Both figures, convey and suggest the regeneration efficiency increases with the increase in the applied current intensity. In Figure 7.12, the trials conducted by *Zhang (2002)* showed that the final regeneration efficiency values improved from ~72% to ~86% when the current intensity increased from 15 mA to 80 mA. *Sun et al. (2013)* obtained comparable findings, with the increase from 1 A to 3 A, there was an 8% increase in the final regeneration efficiency. However, the final results for 2 A and 3 A had proven to be insignificant, with a difference of 1%. The results from *Narbaitz & Cen (1994)* also comply with this trend as there is a significant difference in regeneration efficiency between 10 mA and 100 mA for the entirety of the treatment time. Though, at the treatment time of five hours, 30 mA had a higher regeneration efficiency of ~89%, compared to two out of the three trials using 50 mA: both yielding approximately 87%.

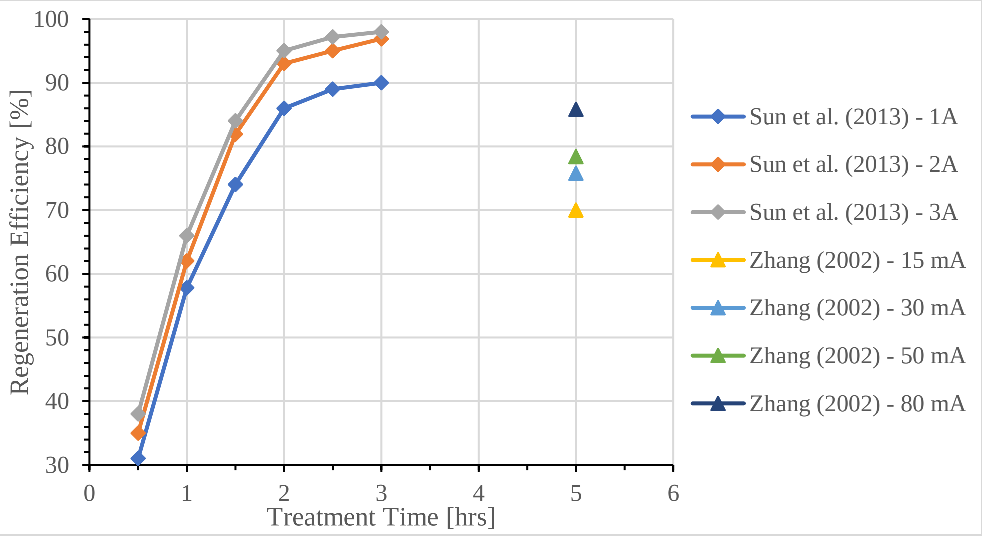


Figure 7.12: Change in Regeneration Efficiency with respect to Current Intensity (a)

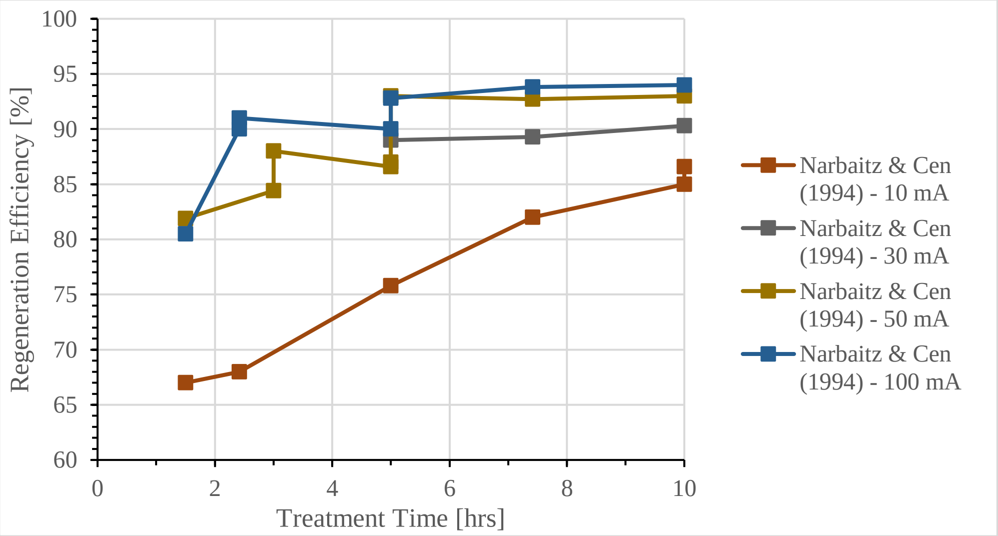


Figure 7.11: Change in Regeneration Efficiency with respect to Current Intensity (b)

Table 7.9: Final Regeneration Efficiency for Regeneration Current Intensity Studies

Regeneration Current Intensity Results		
Study Name	Current Intensity [mA & A]	Final Regeneration Efficiency [%]
Sun et al. (2013)	1 A	90
	2 A	97
	3 A	98
Zhang (2002)	15 mA	~72
	30 mA	~76
	50 mA	~79
	80 mA	~86
Narbaitz & Cen (1994)	10 mA	~86
	30 mA	~91
	50 mA	~92
	100 mA	~93

Figure 7.13 gives an overview of all the regeneration efficiencies obtained from the studies. In the figure, both the highest regeneration efficiency along with the final regeneration efficiency gained from the stated studies are presented. These efficiencies are then separated into the categories of the operational parameters investigated: regeneration time, regeneration cycles and current intensity. It is understood from the figure, for most of the studies, the highest regeneration efficiency is the final recorded regeneration efficiency, which further suggested the increase in value of the operational parameters had a positive effect towards the regeneration efficiency. However, for the regeneration time and current intensity studies, one of the trials for both categories had the final regeneration efficiency lower than the highest recorded regeneration efficiency; inadvertently, both trials belonged to the *Narbaitz & Cen (1994)* study. Moreover, regarding results obtained from the influence of regeneration cycles, the final regeneration efficiency was lower than the highest recorded regeneration efficiency for all the studies within the category. Hence, as priorly stated, the increase in the number of regeneration cycles negatively affects the regeneration efficiency.

Figure 7.13: Final Regeneration and Highest Regeneration Efficiencies for all Studies

Table 7.10: Final Regeneration and Highest Regeneration Efficiencies for all Studies

Electrochemical Regeneration Efficiencies			
Category	Study Name	Highest Regeneration Efficiency [%]	Final Regeneration Efficiency [%]
Regeneration Time	*Zhang (2002)*	~79	~79
	Zhou & Lei (2006)	92	92
	Narbaitz & Cen (1994)	95	~87
Regeneration Cycle	*Zhang (2002)*	~75	~70
	Zhou & Lei (2006)	89	91
	Sun et al. (2013)	94	78
Current Intensity	*Zhang (2002)* – 15 mA	~72	~72
	Zhang (2002) – 30 mA	~76	~76
	Zhang (2002) – 50 mA	~79	~79
	Zhang (2002) – 80 mA	~86	~86
	Narbaitz & Cen (1994) – 10 mA	95	~86
	Narbaitz & Cen (1994) – 30 mA	~91	~91
	Narbaitz & Cen (1994) – 50 mA	~92	~92
	Narbaitz & Cen (1994) – 100 mA	~93	~93
	Sun et al. (2013) – 1 A	90	90
	Sun et al. (2013) – 2 A	97	97
	Sun et al. (2013) – 3 A	98	98

Chapter 8

8. Discussion

As stated prior, the experimental section of this project was altered in order to be finished. The investigation of the adsorption process was mostly completed; however, it was also intended to do a comparative analysis study, to evaluate how to the RNO adsorption model compared with a model using pesticides as the adsorbate. For the electrochemical regeneration investigation, to grasp a greater overview of the process and the affecting parameters towards the regeneration efficiency, a two-level full factorial design of experiments (DoE) with three factors was planned to be conducted. The three factors intended to be investigated were the applied potential, the number of regeneration cycles and the amount of time given for regeneration. After the DoE was conducted, the next step was to launch a method of steepest ascent to find the most optimal operational conditions, which would expectantly yield the highest regeneration efficiency. Similar to the adsorption investigation, a comparative analysis study would have also been conducted to evaluate how the operational conditions found with the RNO model compares when applied to the pesticide model. Since those experiments could not be completed, this discussion chapter will discuss the data that could have been obtained.

Initially, the adsorption process of RNO dye was investigated with differing operating parameters such as the amount of HGR-AC used as the adsorbent, the influence of temperature, and then the combined application of adsorption and applied electric potential. The results from the initial adsorption trials with the different amounts of added adsorbent, as anticipated, showed that the adsorbents possessed a reactivity limit where the adsorption rate decreases and adsorption plateaus. Out of the five amounts of HGR-AC added to the adsorption system, four of the adsorbent amounts showed to reach equilibrium approximately at the same time of 120 minutes, whereas for batch 1 which had 10 mg of added adsorbent, reached equilibrium after 5 minutes. With the increase in the added adsorbent amount, the adsorption rate also increased due to the additional exposed surface area and number of available active site; however, a reoccurring problem of adsorbent rotation may had affected the results. The rotation problem was noticeable when batch 2 (50 mg), which contained five times more HGR-AC content than batch 1 (10 mg), achieved a lower adsorption rate than the rest of the batches. The adsorption rate for this batch was too significant compared to the others, which prompted to repeat the experiments for batch 2. Once the initial adsorption trails were conducted, batch 3 (100 mg) was selected as the model adsorption system for future experiments because there was sufficient dye degradation which yielded a final RNO concentration of 6.87 mg L^{-1}. Another reason batch 3 was selected as a model system, was because the batch was able to reach a n adequately low final concentration, to accommodate for possible further degradation through the optimisation of the operational parameters. Subsequently, during these trials, another problem which could have influenced the results, was the size ratio of the HGR-AC. Even though, the weight of the added carbon was the same for all trials, the number of granular particulates differed: in both amount and size. Therefore, inevitably differing the surface area exposed to the adsorption system.

With regards to the investigation considering the influence of temperature towards the adsorption process, an array of results was obtained. At first it was noticeable that the degradation process for the experiments with applied temperature was not as efficient and did not follow the same degradation trend path as the original (100 mg) experiment at room temperature. This could be the result of the reoccurring problem that occurred during the previous adsorption trials, where there was irregular movement of the adsorbent throughout the experimental trial. From the literature overview in chapter 4, the application of temperature gave varied results: some studies state temperature increases the adsorption rate, and other studies either show the opposite results or temperature had no significant affect towards adsorption. For the experimental runs where temperature was applied at equilibrium (T2) and after equilibrium (T3), the adsorption removal rate seemed to show no significant increase in its adsorption behavior. The batch where temperature was applied from the beginning (T1), was preheated to allow the adsorption process to begin at elevated temperatures; however, there was no record difference in the concentration levels between the investigated batches until 30 minutes, where T1 showed to degrade at a faster rate than T2 and T3. Adsorbate evaporation was another noticeable problem that occurred during the temperature-related experiments, which possibly affected the final yielded results. With the occurrence of evaporation along with the adsorption system not being contained in a sealed pressurised vessel, the amount of adsorbate within the reactor decreased as the experiments continued. As stated in equation 6-9, the volume of the adsorbate is particularly important towards the determination of the adsorption capacity of a system; with the volume of the adsorbate decreasing as the experiment continues, the adsorption capacity in turn decreases as well. Thus, influencing the removal rate of the dye as a result to altering the adsorption capacity. Despite the results, using the current experimental set up and operational parameters, T1 surpassed the degradation reached by the original (100 mg) experiment conducted at room temperature: achieving a lower final RNO concentration of 1.77 mg L^{-1}. However, the results yielded in the temperature investigation cannot be used in addition with either the argument for or against temperature aiding the adsorption process; due to the fact that the conducted experiments also dealt with the unintentional altering of varied adsorbate volumes.

As a connection between the two topics regarding this project, reviewing how applied electric potential affected the adsorption process was of interest. Utilising the electrolytic degradation benefits alongside the current capabilities of the adsorbent should have shown a higher rate of RNO dye degradation. With this part of the investigation, and indications drawn from previous literature review, the current density was a more desired factor to alter rather than the operating voltage. The current density seemed to have more of impact towards the degradation of contaminants; however, with apparatus limitations, the current was kept at a fixed value of 200/300 mA, leaving the operating voltage as the changeable parameter. Before experimentation, backgrounds were noted to observe the difference between the dye degradation caused by electrolytic processes and adsorption combined with applied electric potential. Similar to the temperature experiments, within the first 15 minutes, there was no substantial difference in concentration levels between the original experimental run with 100 mg of HGR-AC and the runs with the aid of electrochemistry. Based on these findings, there seemed to be a delayed response with the addition of both parameter aids, suggesting the there is a treatment time period where additional aids show no significant effect towards the degradation process. Even though both treatment processes operated in unison, the operating voltages of 1 and 2.5 V showed to add no contributive affect, yielding concentrations less than 1 mg L^{-1} from the original (100 mg) experimental run at 0 V. However, the experiment which utilised the maximum operating voltage of 15 V managed to achieve a final RNO concentration of 3.02 mg L^{-1}; a value less than half of the original experiment (6.87 mg L^{-1}). This implies that an applied operating voltage has a positive influence towards the adsorption process but only if the operating voltage is above a certain value. With regards to this investigation, the lowest operating voltage value must be at least 5V before an effect is noticed.

For rate order and adsorption isotherm determination, the initial adsorption experimental trials with altering the amount of added HGR-AC to the adsorption system, was used. Temkin isotherm model was determined as the most suitable fit to describe this system; suggesting the heat of adsorption (ΔH_{ads}) for all molecules linearly decreases with the increase in coverage of the adsorbent surface. The model also assumes there is a uniform distribution of binding energies, up to maximum binding energy. However, the model has a drawback in terms there is no information regarding the maximum adsorption capacity provided. Even though, the Temkin model gave the highest r^2 correlation coefficient, the Freundlich model gave the second highest r^2 correlation coefficient of 0.8679, which suggest there is the possibility of multilayer formation on the surface of the adsorbent. From the rate order models results, the pseudo-second order model was more befitting. Being that the model is pseudo-second order, this can be interpreted as the system being a “surface reaction model” and assumes the transfer of the adsorbate across the solid/solution interface is the slowest step in the entire adsorption process.

Conducting experiments with a target-dye, made it possible to relate the visual observations and findings to that of the behaviour of model contaminants. Regarding the physico-chemical properties of the dye and pesticides, a few of similarities were noticed: the chemical structure, $\log(K_{OW})$ and $\log(K_{OC})$. DMS was the only pesticide which had a similar chemical structure to the dye, albeit with slight variations. Compared to RNO, DMS possess a sulfonamide group and has a NH_2-group instead of a nitroso group (N=O); meaning the bonding energies between the two compounds differ which would reflect towards their oxidative degradation. DMS has the greatest bonding energies of the two, meaning it will have a slower degradation than RNO. The $\log(K_{OC})$ values can have a large error ranges, which vary depending on surrounding environments; with that taken into consideration, the $\log(K_{OC})$ values for DMS and RNO could be within close value proximities, suggesting the dye and pesticides mobility and adhesion to soil and sorbents would be comparable. However, there is a significant difference in the $\log(K_{OW})$ values for the two compounds, with RNO having the greatest value; thus, meaning DMS has a higher affinity to water and is less likely to bind to organics within soils and adsorbents. It is possible to utilise these findings stated earlier and the results from the conducted experiments to somewhat estimate and predict the removal behaviour of DMS to an extent. Due to their similar physico-chemical properties, it can be speculated for DMS to follow similar, if not the same, rate and adsorption isotherms models as RNO. Moreover, it cannot be overlooked that DMS will have a weaker adsorption rate due to the higher bonding energies and a lower log(K_{OW}) value. For this assumption to be confirmed, it is also necessary to investigate other physico-chemical properties which can hinder or aid the adsorption process. As mentioned in chapter 3.1.7, modelling removal behaviours of substances based on their log(K_{OW}) and log(K_{OC}) values has been done in the past but those QSAR models achieved low accuracy. The necessity of gaining more information in relation to the adsorption process is imperative for a QSAR model to predict if the DMS would follow a similar removal trend as RNO.

As stated earlier, the scope of the electrochemical regeneration experimental investigation was altered, and resulted in the form of an intensive literature review. Due to this reason, the investigation is somewhat limited to a selected amount of studies, to keep in relation with the topic of electrochemical regeneration of GAC. The experimental investigation for regeneration was kept similar to the adsorption investigation, by evaluating the influence of different operational parameters towards the regeneration efficiency. The results yielded from the regeneration time trials followed accordingly: the more time allocated for a regeneration cycle, would in turn, increase the regeneration of the adsorbent material and the overall regeneration efficiency. All three studies investigated reached a point in the regeneration process where increasing the time for regeneration was not beneficial for the process, as adsorbent regeneration occurred at a slower rate. *Zhou & Lei (2006)* yielded the highest recorded regeneration efficiency of 92% in the shortest time period of two hours, which could be as a result to using the lowest concentrated regeneration electrolyte. With the review of Table 6.6, regarding the operational conditions of each study, the concentration of the regeneration electrolyte also appeared to be linked with the regeneration efficiency: the regeneration efficiency increased with the decrease in electrolyte concentration. This trend was supported by the other studies, as *Narbaitz & Cen (1994)* used the second highest concentration and *Zhang (2002)* the highest, from which they obtained the second best and lowest regeneration efficiencies, respectively. Due to the lack of regeneration at the finishing hours of the experimental regeneration time, *Zhang (2002)* established five hours to be the most optimum time for regeneration.

Considering the influence of regeneration cycles, the results portrayed the regeneration efficiency to be negatively affected with the increase in the number of regeneration cycles. *Sun et al. (2013)* and *Zhang (2002)* both obtained losses in regeneration efficiency less than

5% but *Zhou & Lei (2006)* had losses greater than 10%. Even though, the difference in efficiency loss could be based on the varying regeneration electrolyte compositions, as *Zhang (2002)* and *Zhou & Lei (2006)* used different concentrations of NaCl and *Sun et al. (2013)* used Na_2SO_4. Another evident reason to the discrepancy was the time given for regeneration. As previously stated, *Zhang (2002)* used five hours for regeneration and the other two studies used two hours. With the combination of both the long regeneration time and the higher concentrated electrolyte composition, the results obtained from *Zhang (2002)* showed to negatively affect the regeneration efficiency. Despite the fact, there is a reduction in the regeneration efficiency with the increase in the number of cycles, the studies have shown electrochemical regeneration to be proficient and capable to obtain sustainably high yields for up to 5 cycles.

Regards to the influence of current intensity towards the regeneration efficiency, the results obtained from the investigation showed unilaterally, the regeneration efficiency increased with the increase in current intensity. With the examined range of 15 mA to 3 A, the increasing trend was apparent. The highest regeneration efficiencies were gained by *Sun et al. (2013)* using 1 A, 2 A and 3 A to yield 90%, 97% and 98%, respectively; with the utilisation of the upper tier current intensities. These findings implied that a large current is required to gain the highest regeneration efficiency. However, the difference between 2 A and 3 A is insignificant, when held in retrospect of practical energy consumption, meaning that 2 A is the most optimal current intensity. In addition, similar to the regeneration cycle experiments, other operational conditions play a factor and affect the final regeneration efficiency, which was clear when *Zhang (2002)* was compared with *Narbaitz & Cen (1994)*. Both studies used similar ranges regarding current intensity, yet there was still a difference in regeneration efficiency that varied from ~13% (50 mA) to ~15% (30 mA). The one factually sourced difference between the two studies was concentration of the regeneration electrolyte.

Chapter 9

9. Conclusion and Perspectives

9.1. Conclusion

The main aim of this thesis was to investigate different operational parameters and their influence towards the combined process of adsorption and electrochemical regeneration; which reflected on the capabilities of the pair's combination to further determine whether the process can be deemed as practical and feasible for water treatment use. The focus was placed on the used o degradation and regeneration efficiencies as the main deciding factors for the evaluation of the investigated operational parameters.

With the investigation regarding adsorption, the experiments were focused on the adsorption kinetics and their behavior. The systematically increased addition of HGR-AC amount to the adsorption system largely improved the removal rate of the dye and the overall removal efficiency. The shift from 10 mg HGR-AC to 500 mg HGR-AC showed an increase of 55% removal efficiency. With the temperature experiments and the varied times of application during the adsorption process, the results obtained were inconclusive due to the occurrence of unintentional adsorbate evaporation which altered the final results. The combination of adsorption and applied electric potential proved to benefit the degradation of RNO with achieving lower final concentrations and a higher removal efficiency of 88%.

The experimentally obtained adsorption capacity of the system increased with the increase in the amount of added carbon; however, when compared with the calculated adsorption capacity, it did not follow the same trend. The experimental kinetic data was analysed using pseudo-first and pseudo-second rate order models, to which the linear pseudo-second order model provided the highest r^2 correlation coefficient. Three isotherm models were used to analyse the experimental isotherm data: Freundlich, Langmuir and Temkin; the data linearly suited the Temkin model the most with the highest r^2 correlation coefficient of 0.9283. The Freundlich model could have also been deemed suitable but the model gave a lower r^2 correlation coefficient of 0.8679.

The results from the electrochemical regeneration of GAC investigation, gained via literature review, showed a variation of regeneration efficiencies can be obtained depending on the operational conditions of the system. Considering regeneration time, all the investigated studies shown an increase in regeneration efficiency with the increase in time to an extent. Current intensity also followed the same trend: the increase in applied current yielded greater regeneration efficiencies. The opposite was observed regarding the number of regeneration cycles, a loss in regeneration efficiency was acquired with the increase in cycles.

The suitability of this method could not be established, as the energy consumption of the experiments could not be recorded. Nonetheless, given optimal conditions, electrochemical regeneration has proven to be suitable enough to obtain high efficiency yields, consecutively for up to five cycles after the adsorbent's first use. The work presented in this thesis can be considered as a preliminary investigation towards determining the practicality of this regeneration method for large-scale applications.

9.2. Perspectives

A drawback for basing the adsorption process on the pseudo-first and pseudo-second order models, is the inability to distinguish the rate limiting step, which is known as the slowest step/series of chemical reactions. This factor can determine the overall rate of the other reactions in the pathway. In order to fulfil this, future work can be focused towards using an intra-particle diffusion model, introduced by Weber and Morris in 1962 [140]. The model proposes that the adsorbate species migrate from the bulk of solution to the internal surface of adsorbent through four stages: (i) transportation from the bulk of solution to the external boundary layer liquid film which surrounds the adsorbent's external surface; (ii) movement across the liquid film, which allows adsorption onto external surface sites of the adsorbent; (iii) migration within the pores of the adsorbent, and (iv) adsorption onto the internal surfaces. Intra-particle diffusion is necessary to accomplish the latter two steps of the model, which can also be referred to as the rate limiting step for the majority of adsorption processes.

Future experimental investigations for this project can be targeted towards the utilisation of more analytical methods, such as high-performance liquid chromatography (HPLC) and solid-phase extraction (SPE). These methods would be expectantly used when conducting experiments where pesticides are the main adsorbate. SPE has proven to be a highly capable extraction and clean-up method that utilises both a solid- and liquid-phase for the separation of the analyte from the sample without impurities before analysis. When conducting the pesticide trials, after performing the SPE method, the target pesticide degradation products and residues would then be separated and determined using HPLC. Additionally, it would be implied to use HPLC after every regeneration cycle to see the transformation and ultimately the termination of the contaminant products.

Reactor design is another recommendation for future research in this topic, as described in this thesis, adsorbate evaporation from the application of temperature affected the adsorption rate and final results. Investigating a series of reactor designs, will aid in the practical feasibility of this regeneration method. Moreover, the potential in exploring reactor designs will also give data into the energy consumption of different design configurations and set-ups; these two considerations are linked as they will facilitate one another towards the final outcome based on practicality.

It was discussed, due to similar physico-chemical properties, a pesticide would follow similar trends paths as gained from the conducted experiments. It would be a priority to experimentally investigate in creating the QSAR models which would require a greater amount of information regarding the physico-chemical properties and adsorption process to confirm whether this assumption to be true; thus, could then change influence how future experiments are planned and conducted. Another advancement for this topic-related research is to investigate whether these methods and operational conditions can be employed to alternative organic contaminants and adsorbent materials. Experimentation with a range of various adsorbent materials, can give more information towards the versatility and application of the electrochemical regeneration process. The findings and results from these experiments can also be used in consideration when determining if this regeneration method is feasible for WTPs and large-scale applications. With this method being optimised for other contaminants such as pharmaceuticals and other micropollutants, the fundamentals of this technology and overall method can then be applied and used in a wider scope of possibilities and treatments.

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10. Appendices

10.1. Appendix I

A generalised scheme of the complete destruction or partial electrochemical conversion of organics on a metal oxide anode (MO_x) into oxidation products is portrayed in **Error! Reference source not found.** [105,107].

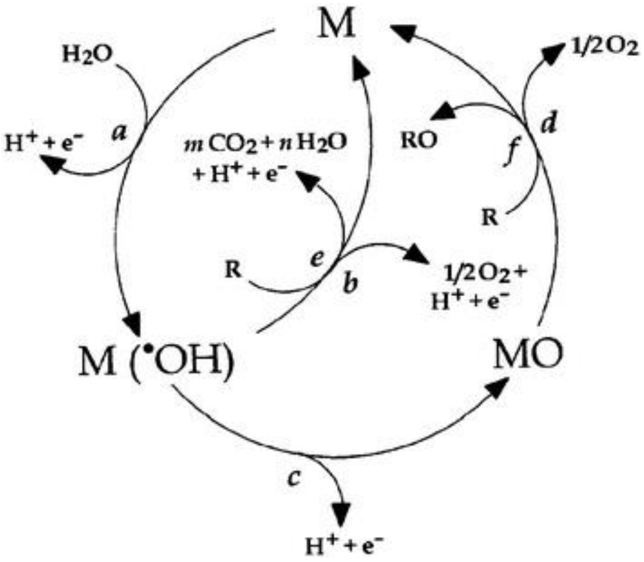

Figure 10.1: Generalised Schematic of the conversion and combustion of Organics on a Metal-oxide Anode [144]

Conducted research by *Comninellis (1994)*, stated there are two cases involved with the generalised scheme: active anodes or non-active anodes. With both cases, the first step in the scheme is the oxidation of water leading to the production of adsorbed hydroxyl radicals, as shown in reaction 10-1 [105,107].

$$\boldsymbol{MO_x + H_2O \rightarrow MO_x(\cdot OH) + H^+ + e^-} \quad [10\text{-}1]$$

In the active anodes case, the first step is then followed by the adsorbed hydroxyl radicals interacting with the oxygen already present in the metal oxide anode (MO_x) to form a higher oxide (MO_{x+1}), as descried in reaction 10-2 [105,107].

$$\boldsymbol{MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^-} \quad [10\text{-}2]$$

From this, it suggests that there is a possibility for there to be two states of active oxygen present on the anode surface: physicosorbed active carbon (adsorbed hydroxyl radicals, ·OH) and chemisorbed active oxygen (higher oxide, MO_{x+1}). In the absence of any oxidisable organics, the physicosorbed and chemisorbed active oxygen produce dioxygen according to reaction 10-3 and reaction 10-4 [105,107].

$$\boldsymbol{MO_x(\cdot OH) \rightarrow \frac{1}{2}O_2 + H^+ + e^- + MO_x} \tag{10-3}$$

$$\boldsymbol{MO_{x+1} \rightarrow MO_x + \frac{1}{2}O_2} \tag{10-4}$$

Rosenthal was a scientist whose work and research provided evidence for the last route of oxygen evolution with Platinum oxide (PtO_x) as an active anode, using 18O as a type of tracer molecule to show that a portion of the evolved gas comes from oxygen already present in the oxide film. Since then, this scope of research was tested with various electrodes acting as active anodes such as ruthenium oxide (RuO_2), iridium oxide (IrO_2), nickel cobaltite ($NiCo_2O_4$), nickel oxyhydroxide (NiOOH) and graphite [105,107].

With consideration of non-active anodes, the present hydroxyl radicals weakly interact with the electrode surface. Oxidation of organics mediated by hydroxyl radicals may result in completely oxidised products such as CO_2, as shown in reaction 10-5 [105,107].

$$\boldsymbol{R + MO_x(\cdot OH) \rightarrow CO_2 + zH^+ + ye^- + MO_x} \tag{10-5}$$

As viewed in the generalised scheme shown in **Error! Reference source not found.**, R represents the fraction of an organic compound containing no heteroatoms, meaning the compound requires one oxygen atom to be fully converted to CO_2. This reaction competes with the side reaction of hydroxyl radicals to oxygen, without any participation of the anode surface, also referred to as selective oxidation as shown in reaction 10-6 [105,107].

$$\boldsymbol{R + MO_{x+1} \rightarrow RO + MO_x} \tag{10-6}$$

10.2. Appendix II

The results from the EO experiments of the dye are displayed in Figure 10.2 and Table 10.1. From the figure, it is evident, that the EO process was not as strong as the adsorption process. Table 10.1 shows the maximum removal efficiency of the dye through EO was 18% achieved using 15 V, which is 55% less that the original experiment with 100 mg of HGR-AC at 0 V. The dye degradation increased with the increase in operating voltage. However, the increase in degradation can be deemed insignificant for the voltages ranging between 1 – 5 V because there is no apparent change in removal efficiency; from the results, the figure and table state that 1 V managed to degrade the dye lower than 2.5 V. It should also be noted that there was no constant degradation for all operating voltages used: there was a fluctuation of results for each degradation line.

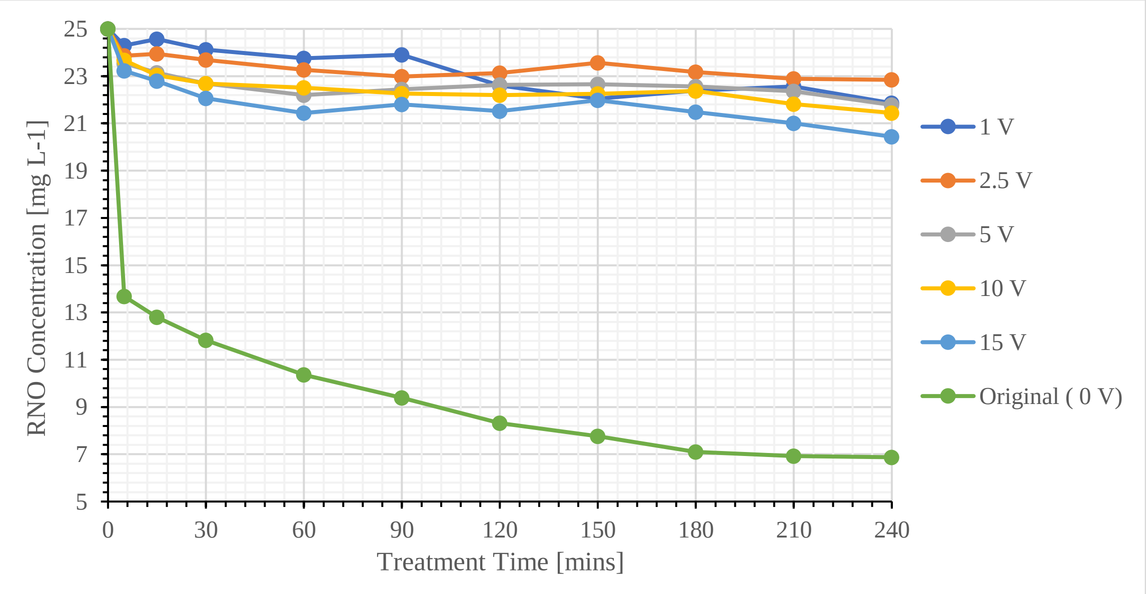

Figure 10.2: EO of RNO through at Different Voltages

Table 10.1: Final Concentrations and Removal Efficiencies for EO of RNO

Operating Voltage [V]	Final RNO Concentration [mg L-1]	Removal Efficiency [%]
1	21.857	13
2.5	22.843	9
5	21.786	13
10	21.403	14
15	20.437	18
Original (0)	6.873	73

10.3. Appendix III

Figure 10.3 indicated the $\log(q_e)$ intercept increased with the increase of adsorbent added to the system. A similar trend was also viewed in Table 10.2, the experimentally obtained q_e values noticeably increase with the increased amount of adsorbent. Table 10.2 additionally shows the correlation coefficients, r^2; from which, shown that batches 2 – 5 suitably fit the pseudo-first order model in linear form, due to showing somewhat high r^2 values. However, batch 1 does not possess a high correlation coefficient which suggested that this linear model was not befitting.

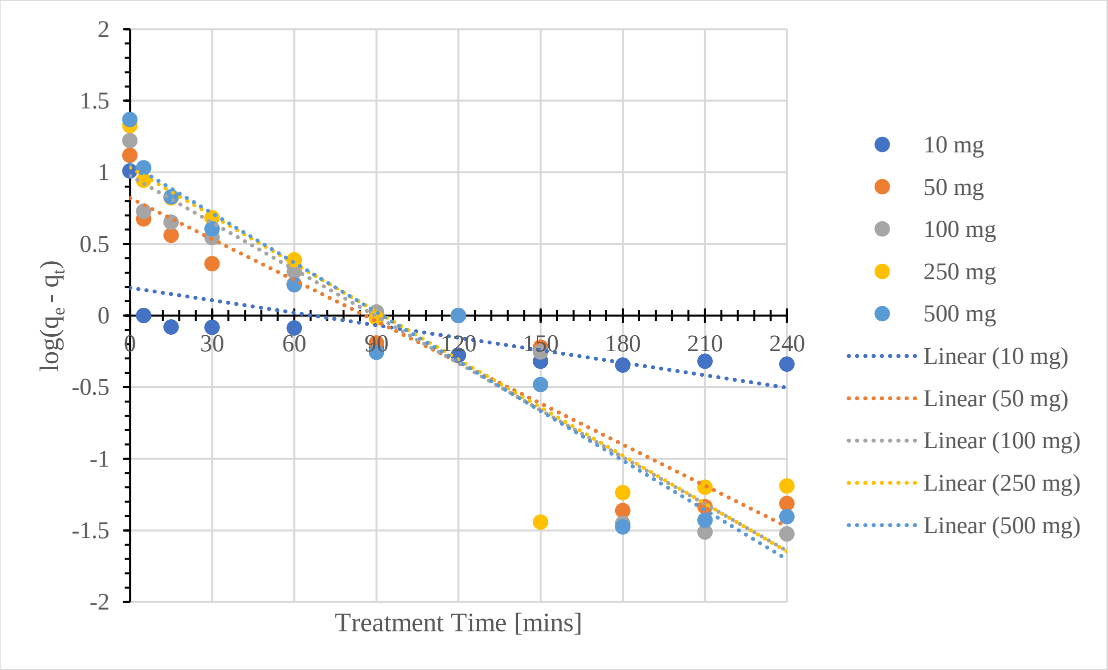

Figure 10.3: Pseudo-First Order Adsorption Kinetics of RNO onto Different Amounts of HGR-AC (10 mg – 500 mg)

Table 10.2: Kinetics Parameters for Adsorption of RNO using Pseudo-First Order Linear Equations

Carbon Amount [mg]	$q_{e,\,exp}$ [mg g^{-1}]	k_1 [min^{-1}]	r^2
10	10.2267	0.0029	0.4154
50	13.1300	0.0096	0.9078
100	16.6767	0.0109	0.9285
250	21.2600	0.0112	0.8919
500	23.3733	0.0115	0.9367

$Q_{e,\,exp}$: experimentally calculated amounts of adsoprtion at equilibrium; k_1: pseudo-first order rate constant; r^2: correlation coefficient