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DESULPHURISATION OF PETROLEUM DISTILLATES USING ADSORPTION METHOD

Prepared by

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A Research Report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in partial fulfilment of the requirements for the degree of Master of Science in Engineering

(50/50 course)

August 2014, Johannesburg, South Africa

Declaration

I declare that this study is my own unaided work. It is being submitted for the partial fulfilment of the requirements of Master of Science degree in Engineering to the University of the Witwatersrand, Johannesburg. The report has not been submitted before for any degree or examination in any other University.

……..

Signature of M.J. Nkosi

……. day of August 2014

Abstract

Experiments were conducted to investigate the applicability of activated carbon in removing sulphur from petroleum distillate at different sulphur concentrations. The study was therefore divided into two: The first part was the desulphurisation of a diesel stream containing 5200 mg/kg sulphur. This was referred in this report as Case 1. On a typical refinery, this is the feed stream of the hydrotreater unit. The second part of the study was the desulphurisation of a diesel stream containing 120 mg/kg sulphur. This sulphur concentration referred to case 2, which resembles an exit stream of the hydrotreater unit on a typical refinery.

In Case 1, the activated carbon managed to reduce the sulphur content from 5200 mg/kg to 3390 mg/kg. Only about 35% of the sulphur was removed. In Case 2 however, the diesel stream was desulphurised from 120 mg/kg to 22 mg/kg. About 82% of the sulphur was removed from the feed-stream depicting activated carbon's desulphurisation capability when dealing with lower sulphur concentration petroleum distillate.

Adsorption isotherms and kinetics models were applied to the experiment data to understand the extent and rate of sulphur adsorption on the surface of the activated carbon. The applicability of both adsorption isotherm and kinetics models to the experiment data were evaluated by the correlation coefficient (R^2) value with 5% statistical significance. The Langmuir isotherm model fitted well Case 1 experiment data. The obtained Langmuir isotherm constant (K_L) was 1.19 X 10^{-4} g/mg. This K_L value was lower compared to Case 2 value of 0.0123 g/mg. This indicated that each sulphur molecule on activated carbon adsorption surface had a better equal adsorption activation energy in Case 2 than in Case 1. In Case 2, the obtained Freundlich isotherm constants, K_F and n were 5.22 and 1.04 respectively. The n value for Case 2 was higher than Case 1 n value (1.04 vs 0.55). This clearly indicated that the sulphur molecules adsorption intensity on the surface of the

activated carbon was higher in Case 2 than in Case 1. The K_F value for both cases indicated the activated carbon adsorptive capacity. Pseudo-first-order kinetic model fitted well case 2 experiment data. The kinetic rate constant obtained for Case 2 was 0.206 min^{-1}, whilst the kinetic rate for Case 1 was 0.0423 min^{-1}. This indicated a slower sorbate uptake rate in the higher sulphur concentrated diesel stream than the lower concentrated stream. It is well understood that no adsorption processes are exactly the same as many studies have indicated, however these comparisons of these Case's isotherms and kinetics were highlighted to indicate the impact of higher sorbate concentration in the desulphurisation of petroleum distillate. For both case 1and 2, it was established that the adsorption of sulphur on activated carbon was particle diffusion in nature.

The results of the study therefore indicated that application of adsorption desulphurisation method seem not capable to achieve ultra-low sulphur specification when treating diesel feed with high sulphur content. On the other hand, the results of the study also revealed that there is an opportunity for synergistically employing activated carbon adsorption in combination with hydrodesulphurisation to achieve low sulphur diesel specification.

Dedications

This study is dedicated to my family for all the support throughout this study period.

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Nomenclature

C_t - solute concentration at time t, mg kg^{-1}

C_0 - input solute concentration, mg kg^{-1}

C_e - equilibrium concentration of solute, mg kg^{-1}

K_F - Freundlich constant, kg mg^{-1}

K_L - Langmuir constant, kg mg^{-1}

k_1 - first-order adsorption rate constant of Lagergren model, min^{-1}

n - Freundlich constant related to adsorption intensity

q - quantity of adsorbed sulphur on adsorbent surface, mg g^{-1}

q_e - equilibrium adsorption capacity, mg g^{-1}

R^{2} - correlation coefficient

t - time, min

V - volume of a solution containing solute, ml

W - mass of adsorbent, g

List of abbreviations

Bio-desulphurisation - BDS

Dimethylbenzothiophenes - DBT

Hydrodesulphurisation – HDS

Intellectual property - IP

Oxidation desulphurisation - ODS

Scanning Electron Microscope – SEM

Chapter 1: Research background

1.1 Introduction

Globally, the surge in public concerns about the environment is causing the increase in number and stringency of legislative actions. The petroleum refining industry, perceived as one of the largest source of pollution both direct and indirect, is on the front line of the battle for achieving environmentally friendly and sustainable operation. The pressure is mounting on the refineries to produce cleaner products while at the same time to minimize or completely eliminate the negative impact on the environment (Muzic *et al.*, 2009). Investments are made on alternative energy research and development with the intent of lowering the environmental impact. However at the moment, oil and coal remain the main source of energy hence the drive to minimise the sulphur emitted during processing of these energy sources. Kim *et al.*, (2010) proclaim that the estimated amount of oil deposits continually dwindles and the price of oil continues to increase, it has therefore become necessary to refine crude oil that contains high sulphur content. The sulphur content in crude oils has a direct relationship to the percentage of sulphur found in fuel oils; most of the sulphur in crude oils ends up in the distillates (Yazu *et al.*, 2001). This therefore, means that besides the environmental need to minimise sulphur content in oil, there is also a financial justification.

In refineries, the removal of sulphur has been primarily through hydrodesulphurisation (HDS) method. However, Kim *et al.*, (2010) argues that it is difficult to reduce sulphur levels using the current HDS process because of the very low reactivity of the HDS catalysts towards sulphur compounds. An increase in the reactor size and hydrogen consumption is required to

achieve high levels of desulphurization. Therefore HDS may be very costly to employ in order to achieve euro *5* standard requirements.

This study aims at determining whether using adsorption desulphurisation after HDS can lower diesel sulphur content to less than *10 ppm* thus meeting euro *5* specifications. Since removing refractory sulphur compounds, such as benzothiophenes (BT), dibenzothiophenes (DBT's) and their alkylated derivatives which are usually, in large amounts, present in diesel fuel, is met with high degree of difficulty in HDS method, adsorption method is a suitable alternative (Javadli *et al.,* 2012). Adsorptive desulphurization provides an alternative technology of particular interest due to its low-energy consumption, the availability of regeneration of spent adsorbent and the ambient operation temperature and pressure (Xiong *et al.,* 2011). Muzic *et al.,* (2009) describes adsorption as an effective process in the selective removal of low-concentration materials from liquids. It enables achievement of ultra-low sulphur concentration while incurring the least amount of negative effects on other fuel properties. Furthermore, adsorption does not consume hydrogen and can be operated at ambient or rather low temperature and pressure.

1.2 Justification

Sulphur is the most abundant element in petroleum after carbon and hydrogen. The average sulphur content varies from *0.03* to *7.89 mass%* in crude oil (Javadli *et al.,* 2012). Environmental concerns have driven the need to remove sulphur impurities from petroleum products. Sulphur impurities are of particular interest because of their contribution to acid rain formation and airborne particulate material. It has been reported that sulphur in the form of SOx is harmful to the environment (Kjartansson, 2011). Figure 1.1 depicts an example of sulphur's harmful effect on the environment.



Figure 1.1: Forest in Poland destroyed by sulphur emissions. (Nehlsen *et al.*, 2005)

Sulphur also poisons the catalyst in catalytic converters and thus reduces its efficiency (Kanyoke, 2004). Within the refining process itself, sulphur, even in extremely low concentrations, poisons the noble metal catalysts (platinum and rhenium) in the catalytic reforming units that are used to upgrade the octane rating of the naphtha streams (Kanyoke 2004).

An ever-growing and explosive demand of petroleum products justifies constant search of innovative methods to optimize petroleum products quality. Sulphur adsorption is one of the most common HDS alternative methods for the removal of residual sulphur in fuel (Adeyi *et al.*, 2012). According to Khan, *et al.*, (2012), adsorption process is recognized as an important process in the field of separation technology. This study is significant because petroleum products standards (Euro *3, 4&5*) require lesser sulphur content in diesel thus minimizing environmental impact. The success of applying adsorption desulphurization in series with the hydrotreater can be of great importance in countries like South Africa who are yet to comply with the Euro *5* standard.

1.3 Problem statement

Globally, refineries are in a quest to lower sulphur content in petroleum products. Hydrodesulphurisation has been widely used in refineries because of its substantial capability to remove sulphur. However, new legislations driven by environmental friendly operations require ultra-low sulphur content in petroleum distillates. It is difficult to achieve low sulphur contents through HDS due to high operations conditions and high hydrogen consumption. This has triggered a need to investigate alternative technologies to achieve Euro 5 standards. Due to environmental issues that sulphur poses to societies as discussed in section 1.2, it is imperative for petroleum companies to lower sulphur content in petroleum products to remain competitive and sustainable. Most desulphurisation alternative technologies to hydrotreater are generally not commercially successful. At the same time, hydrotreater, on its own, is unable to achieve Euro 5 specifications. It is therefore imperative to investigate the application of the adsorption method in series with the hydrotreater to achieve ultra-low sulphur content in petroleum distillates.

1.4 Hypothesis

Activated carbon adsorption method can remove sulphur from petroleum distillates. Activated carbon has sulphur selectivity from the petroleum distillates. The sulphur content on the petroleum distillate has a direct impact on the activated carbon's capability to reduce the sulphur to required specification. It is expected that the use of adsorption desulphurisation method in series with the hydrotreater in treating diesel should yield ultra-low sulphur specification of *10 mg/kg*.

1.5 Research objectives

The main objective of this research is to evaluate the possibility of applying adsorption desulphurisation after hydrotreater to achieve ultra-low sulphur specifications. The specific research objectives are:

1) To investigate whether adsorption desulphurization method can lower sulphur content of a diesel feed with sulphur content above 5000 mg/kg to less than 10 mg/kg specifications.

2) To determine whether adsorption desulphurisation method used after hydrodesulphurisation can lower diesel sulphur content to less than 10 mg/kg.

Chapter 2: Literature review

2.1 Introduction

In this chapter, the literature applied to the study was discussed. Sulphur organic compounds were discussed to indicate why adsorption on activated was a suitable method for reducing sulphur to euro 5 standards. The reasons why activated carbon was chosen as an adsorbent was clarified. Other sulphur removal alternative methods were also discussed and their limitations highlighted. This secondarily highlighted how better suited the adsorption method on activated carbon was to the rest of the alternative methods. Literature on adsorption isotherms and kinetics was discussed to indicate how these adsorption models were applied to the experiment data to understand the extent and the rate of the adsorption. Even though adsorbent regeneration was not part of the study scope, however a practical possible regeneration method was discussed.

2.2 Organic sulphur compounds and activated carbon

The sulphur compounds can be found in two forms: inorganic and organic. Inorganic sulphur, such as elemental sulphur, hydrogen sulphide (H_2S) and pyrite can be present in dissolved or suspended form. Organic sulphur compounds such as thiols, sulphides, and thiophenic compounds represent the main source of sulphur found in crude oil (Javadli *et al.*, 2012). Various materials are used to produce activated carbon and some of the most commonly used are agriculture wastes such as coconut shell, pistachio shell, saw dust, walnut shell, tropical wood and almond shell (Kim *et al.*, 2010).



Figure 2.1: An example of coconut shell activated carbon

Several studies have revealed that activated carbon is capable of performing adsorption sufficiently and one of many examples is effective removal of dyes and other pollutants from aqueous solutions (Hameed *et al.,* 2008). Activated carbon was chosen as an adsorbent due to its capability to selectively remove DBT's from fuel without changing the chemical characteristics of the fuel. Also, activated carbon is capable of removing sulphur from fuel under atmospheric conditions thus rendering the process relatively cost efficient.

2.3 Some of the current technologies for desulphurisation of crude oil

2.3.1 Hydrodesulphurisation (HDS)

Hydrodesulphurisation is one of the catalytic desulfurization processes, which aims at turning organic sulphur compounds into H_2S using H_2 as the reactant in the presence of metal catalysts operating at high temperature and pressure. The resultant hydrogen sulphide is then removed from the system (Lin et al, 2010).

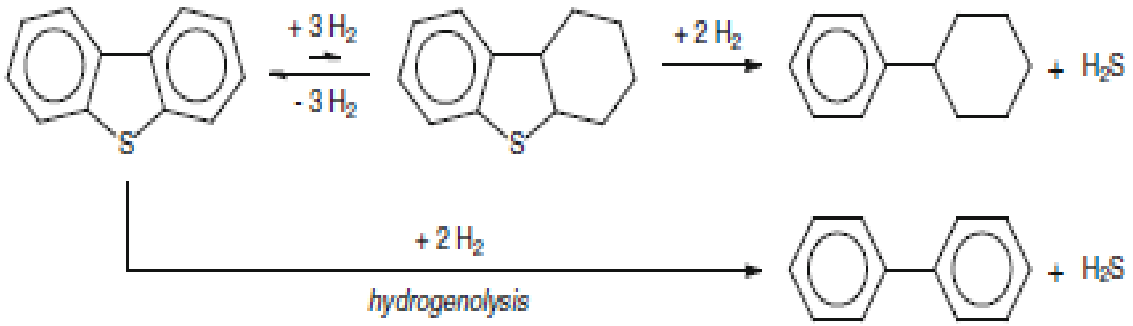


Figure 2.2: HDS hydrogenation and hydrolysis pathways. Javadli *et al.*, (2012)

Hydrodesulphurisation is a widely used process in crude refining industry. In the past two decades petroleum refining has changed extensively and hydrotreaters in particular, are now occupying a central role in modern refineries and more than *50%* of all refinery streams now pass through hydrotreaters for conversion, finishing, and pre-treatment purposes (Song *et al.*, 2006). Most HDS operations also remove nitrogen compounds and some metal impurities (Nehlsen *et al.*, 2005). Some studies reveal that Ni/ZnO is widely used to remove sulphur species because of its high-sulphur binding capacity and favourable thermodynamics at moderate temperature (Zhang *et al.*, 2013). Hydrodesulphurisation, however, consumes a lot of hydrogen and has to be operated at high temperatures and pressures. Also much higher activity and selectivity of HDS catalysts should be designed for the removal of refractory sulphur compounds in petroleum light products (Sakanishi *et al.*, 2003). Therefore, maintaining these operations requirements leads to high operating costs. Furthermore, the challenge with hydrodesulphurisation is that it is difficult to achieve ultra-low sulphur contents which are the requirements of the latest euro *5* specifications.

2.3.2 Bio desulphurisation (BDS)

According to the principle of enzyme catalysis for implementing the specific reaction for C—S bond cleavage performed by micro biological flora, sulphides in crude oil can be turned

into elemental sulphur that can be removed. In the process of desulphurization, the sulphur containing pollutants are transformed into sulphides and H_2S by biological reduction, and the elemental sulphur can be removed via the process of biological oxidation (Lin et al, 2010). Biological removal of sulphur has several limitations that prevent it from being applied today. The metabolism of sulphur compounds is typically slow compared to chemical reactions. Also, large amounts of biomass are needed (typically *2.5 g* biomass per g sulphur), and biological systems must be kept alive to function, which can be difficult under the variable input conditions found in refineries (Nehlsen *et al.*, 2005). Lin *et al.*, (2010) also highlights challenges associated with bio-desulphurisation method; firstly, this process is not very efficient and secondly one kind of bacteria can only remove one or few sulphides. Clearly more research is still needed on this method to enable sufficient commercialisation.

2.3.3 Oxidative desulphurisation (ODS)

Oxidative desulphurisation is one of the petroleum desulphurisation technologies that has been given much interest recently due to its mild condition and does not need H_2. Sulphur-containing compounds are oxidized using a selective oxidant to create compounds that can be preferentially extracted from light oil due to their increased relative polarity (Zhao, 2003). The bivalent sulphur in the organic compounds expands its shell to accommodate oxygen without the need to break carbon-sulphur bond and this makes the oxidised sulphur highly polar (Yao *et al.*, 2004). Oxidative desulphurisation is a process based on the removal of heavy sulphides, usually in the form of polynuclear aromatics where one ring is a thiophene structure (Nehlsen *et al.*, 2005). In ODS, these compounds are oxidized by adding one or two oxygen atoms to the sulphur without breaking any carbon-sulphur bonds, yielding the sulphoxide and sulphone, respectively. The process is followed by extraction which is accomplished by contacting oxidized distillate with a non-miscible solvent that is selective

for the relatively polar oxidized sulphur- and nitrogen-containing compounds (Zhao *et al.*, 2003).

The type of ODS that is relevant to heavy oil conversion, is oxidation of the sulphur in sulphide and thiophenic compounds to sulphoxides and sulphones (Javadli, 2012).

$$R-S-R' + {}^1/_2O_2 \rightarrow R-(SO)-R'$$
$$R-S-R' + O_2 \rightarrow R-(SO_2)-R' \qquad 2a$$

The sulphoxides and sulphones have two properties that are different from the unoxidised sulphur compounds and that facilitate desulphurisation. The sulphoxides and sulphones are more polar, which increases selectivity during solvent extraction. Also, the C–S bond strength is decreased when the sulphur is oxidized (Javadli *et al.*, 2012). According to Ali *et al.*, (2006), oxidative desulphurisation has the potential of being widely developed for commercial use or as an additional process to hydrodesulphurisation for removing refractory sulphur compounds. Furthermore, a study conducted by Campos-Martin *et al.*, (2010) envisaged the oxidative desulphurisation method as having potential of reducing operating costs by 15%. It has been however reported that ODS method is yet to be successfully commercialised.

2.3.4 Adsorption desulphurisation

Sulphur adsorption on activated carbon is a physical as well as reactive process. In physical adsorption, the sulphur compounds are not chemically altered by the separation. Whereas reactive adsorption, involves a chemical reaction between organosulphur compounds and solid sorbent surface. Sulphur is usually attached to the sorbent as a sulphide (Javadli, 2012). The interaction between the sulphur compounds and the adsorption sites on the adsorbent should be selective and suitable in strength. Too strong interaction between them will cause a

difficulty in the subsequent regeneration process while too weak interaction may probably lead to low adsorption selectivity and low capacity (Sun *et al.,* 2003).

Metal ion-exchange Y zeolites have also been shown to effectively remove sulphur compounds under ambient conditions. However, the sulphur adsorption capacity depends on the composition of the fuel. Adsorptive removal of sulphur compounds from liquid commercial fuels has been widely investigated using various different adsorbents such as porous carbon materials, metal impregnated oxides and zeolite. Among these absorbents, Ag-Y and Cu-Y zeolites have been shown to have a particularly high adsorption capacity and selectivity for thiophene and its derivatives via π-complexation (Kim *et al.,* 2010). The hydrotreater is limited in treating benzothiophenes and di benzothiophenes, especially DBTs having alkyl substituents on their 4 and / or 6 positions, as indicated in Figure 2.3.

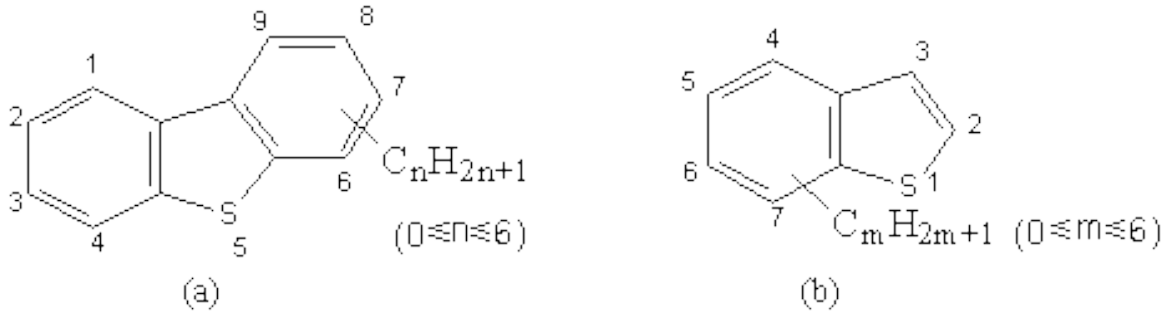


Figure 2.3: Structure of (a) DBTs and (b) BTs in actual light oils. Zhao *et al.*, (2003)

Muzic *et al.,* (2009) describes adsorption as one of the most promising processes for deep desulphurization of diesel fuels. He further describes this process as effective in the selective removal of low-concentration materials from liquids. Furthermore, Xiong (2011) articulates that adsorptive desulfurization provides an alternative technology of particular interest due to its low-energy consumption, the capability of regeneration of spent adsorbent and the ambient operation temperature and pressure.

Previous studies have suggested that the sulphur removal capacity can be improved by metal or metal halide impregnation into adsorbents although the feed composition, sulphur content and process conditions are different according to Kim (2010). The media in which adsorption occurs also varies largely from one case to another. Therefore, it is difficult to make a parallel comparison between different adsorption systems. Al Zubaidy (2013) and his co-workers conducted research which revealed that *13X* zeolite have the highest capacity for sulphur at low concentration range and activated carbon at higher concentration range.

2.4 Adsorption isotherms

The adsorption equilibrium can be described by adsorption isotherms. An adsorption isotherm is a constant temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent and the equilibrium concentration of adsorbate in the solution. Freundlich and Langmuir adsorption isotherms were used to model the equilibrium adsorption data obtained for adsorption of sulphur from diesel on activated carbon. Adsorption is usually described through an isotherm, Okeola *et al.,* (2010) claim. He further claims that the adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Freundlich and Langmuir isotherms were used to understand the extent and degree of favourability of adsorption.

The adsorption capacities at time t (q_t) and equilibrium adsorption capacities (q_e) at different concentrations were determined by (Jiwalak *et al.,* 2010):

$$q_t = \frac{(C_o - C_t)V}{W} \qquad 2b$$

$$q_e = \frac{(C_O - C_e)V}{W} \qquad 2c$$

Where Co, C_t, C_e (mg/L) are the liquid-phase concentrations of sulphur in diesel at initial, at time t and at equilibrium, respectively. V is the volume of the solution and W is the mass of dry adsorbent used (g).

The Langmuir and Freundlich parameters were determined and correlation coefficients were calculated. The Freunflich isotherm is expressed as (Hameed *et al.*, 2008):

$$q_e = K_F\, C_e^{1/N} \qquad 2d$$

In a linear form, equation 2d can be expressed as:

$$\log q_e = \log K_F + \frac{1}{N} \log C_e \qquad 2e$$

Where q_e is the equilibrium amount adsorbed per gram of the adsorbent, C_e is the equilibrium concentration, while K_F and 1/n are constants. K_F is a function of energy of adsorption and temperature and is a measure of adsorptive capacity, and 1/n determines intensity of adsorption.

The Langmuir isotherm can be expressed as (Kumar *et al.*, 2009):

$$q_e = q_{max}\, \frac{K_L C_e}{1 + K_L C_e} \qquad 2f$$

The linear form of equation 2f is:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \qquad 2g$$

Where q_{max} is the theoretical maximum adsorption capacity of the adsorbent (mg/g) and K_L indicates a binding constant which is related to the heat of adsorption. All the constants are specific to experiment conditions and the adsorbent type. The plots of $1/q_e$ versus $1/C_e$ and

Log q_e versus Log C_e were made to test the Langmuir and Freundlich adsorption models respectively. In each case related respective constants were determined. The applicability of the isotherm models was evaluated by the correlation coefficients, R^2 value of each plot. Linear regression was carried out to establish its statistical significance at 5% level of significance (95% confidence level). The higher the R^2 value, the better fit to the model.

2.5 Adsorption kinetics

Predicting the rate at which adsorption takes place for a given system is a crucial factor in adsorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics (Ho *et al.*, 2006).

Kinetics studies were carried out to measure the rates of adsorption under various experimental conditions. This enabled the researcher to determine the influence of variables like input sulphur concentration on the rates of reaction. Kinetics studies also help to determine the time requirement for the attainment of equilibrium during the adsorption process (Mittal *et al.*, 2006). Kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface (Ho *et al.*, 1999). The mechanism and the efficiency of the adsorption process can be inferred from their kinetic studies. Consequently, the kinetic data was processed in order to understand the dynamics of adsorption process in terms of order of rate constant.

Pseudo-First-Order: Kinetic data were treated with the Lagergren pseudo-first-order kinetic model. In linear form, the model can be expressed as (Lam *et al.*, 2008):

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t \qquad 2h$$

Where q_e is the amount of sulphur adsorbed (mg/g) at equilibrium whereas q_t refer to the amount of sulphur adsorbed at any time, t (min). K_1 is the equilibrium rate constant of pseudo-first-order adsorption in min^{-1}. A linear graph of log (q_e-q_t) versus t was plotted where K_1 and q_e were obtained.

Pseudo-Second-Order: Kinetic data were further treated with the typical pseudo-second-order kinetic model and the linearized equation is (Lam et al., 2008):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad 2i$$

Where K_2 is the equilibrium rate constant of pseudo-second-order model (g $mg^{-1}min^{-1}$).

To enhance the interpretation of the kinetics, steps in the adsorption process had to be identified through mathematical methods. Successive steps involved in the adsorption of an organic or inorganic by an adsorbent include (Mittal *et al.*, 2006):

i) Transport of the adsorbate to the external surface of the adsorbent i.e. film diffusion.

ii) Transport of the adsorbate within the pores of the adsorbent except for a small amount of adsorption which occurs on the external surface i.e. particle diffusion.

iii) Adsorption of the adsorbate on the interior surface of the adsorbent.

A quantitative treatment of the sorption dynamics was determined by the expression (Reichenberg *et al.*, 1953):

$$B_t = 2\pi - \frac{(\pi^2 F)}{3} - 2\pi \left(1 - \frac{\pi F}{3}\right)^{0.5} \qquad 2j$$

Where *F* is the fractional attainment of equilibrium at time t and is obtained using equation 2k.

$$F = \frac{Q_t}{Q_\infty} \qquad 2k$$

Where Q_t and Q_∞ are amounts adsorbed after time t and after infinite time, respectively. Reichenberg's (1953) table and equation 2h were used to determine *F* and corresponding B_t values as depicted in table D in appendixes. In this study, the linearity test of B_t versus t plots have been employed to distinguish between film and particle diffusion controlled rates (Shady *et al.*, 2012).

2.6 Regeneration of the Adsorbent

Regeneration of the adsorbent is important in completing the adsorption process loop. Kim (2010) conducted experiments to investigate the efficiency of regenerating the spent adsorbents. The saturated adsorbent was washed with toluene to remove the sulphur compounds that were adsorbed to the adsorbents. Toluene consists of one benzene ring and one methyl functional group that can form a π-complexation with the metal halide in the spent adsorbent (Kim *et al.,* 2010). This phenomenon enables sulphur compounds adsorbed in the spent adsorbents to be removed. The toluene treated adsorbent can be dried under vacuum and reactivated under high temperatures. Figure 2.3 exhibits an overview of the regeneration process applied to hydrotreater in series with the adsorber.

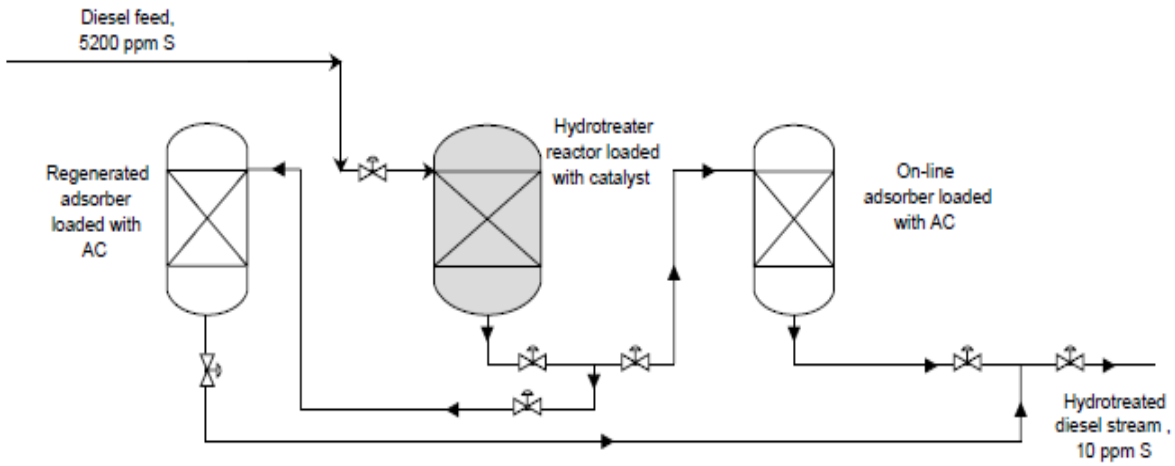


Figure 2.4: Regeneration overview

Figure 2.4 depicts a practical possible application of a hydrotreater in series with the adsorbers. When one adsorber undergoes regeneration, the other is commissioned and put online and vice versa. In addition, toluene is readily available and relatively less costly.

2.7 Chapter summary

Organic sulphur compounds were discussed. The chemical characteristics of activated carbon indicated its capability to reduce sulphur from petroleum distillates to euro 5 specifications. This ancillary explained the activated carbon choice as an adsorbent. How the adsorption isotherms and kinetics models were applied to the experiment data was indicated. It was fundamental to note that no adsorption processes are the same. Therefore both adsorption isotherms and kinetics constants are experiment specific. As regeneration is a crucial step in adsorbent selection, it has been established that toluene's physico-chemical characteristics enables it to easily wash off sulphur from activated carbon without interfering with the fuel's chemical characteristics. Therefore toluene's capability, availability, practicality in application and less cost justified why it was a preferred method. Further studies on the regeneration method would be recommended though.

Chapter 3: Experiment and Research Methodology

3.1 Introduction

The purpose of this chapter was to discuss the experiment resources, materials, procedure and analysis techniques applied to get the research results.

3.2 Material

The adsorbent used was Aquasorb CP3 activated carbon synthesised from coconut shell. The adsorbent was obtained from Sasol polymers plant whose supplier could not be mentioned due to confidentiality agreement. Due to intellectual property (IP) and non-disclosure agreements between Sasol and the supplier, characteristics of the activated carbon could not be disclosed. Therefore, it was necessary to determine the characteristics of the activated carbon prior to using it. The analysed initial characteristics were: particle diameter, 0.022–0.250 mm, bulk density, 0.48 g cm^{-3}, surface area, 788.8 m^2 g^{-1}, pore volume, 0.414 cm^3g^{-1}, ash content, 2.6%. It was important to know these characteristics of the activated carbon used as they affect its adsorption capability. Typical physical and chemical properties of diesel fuels that were used are presented in Table 3.1.

Table 3.1: Physical and chemical properties of a typical diesel fuel

Property	Value
Cetane index	46.0
Density at15°C, kg m^{-3}	820.0
Polycyclic aromatic hydrocarbons, wt. %	2.1
Total sulphur, mg kg^{-1}	5200 HDS feed, 120 HDS outlet

Ignition point, °C	>55
Kinematic viscosity at 40°C, $mm^2 s^{-1}$	3.98
vol. % distilled until 250 °C	<40
Distillation: vol. % distilled until 300 °C	75
end of distillation, °C	342

The diesel fuel used in the study together with its characteristics was obtained from Natref Refinery. Two 5 litre samples were obtained. The first sample was from the hydrodesulphurisation reactor feed containing 5200 mg of sulphur per kg of diesel. This sample was used to conduct case 1 experiments. The second sample was from the hydrodesulphurisation reactor outlet (hydrotreated diesel) containing 120 mg of sulphur per kg of diesel fuel. This sample was used to conduct case 2 experiments.

3.3 Experimental procedure

A batch adsorption experiment set-up was prepared to carry out diesel fuel desulphurisation. The schematic of the experiment set-up is depicted in figure 3.1. The experiments were conducted in two sets. The first set (Case1) was the adsorption treatment of hydrodesulphurisation reactor feed containing 5200 mg of sulphur per kg of diesel. The second set (Case2) was the adsorption treatment of the hydrodesulphurisation reactor outlet stream containing 120 mg of sulphur per kg of diesel fuel.

Case 1 experiments were conducted specifically to determine whether adsorption desulphurisation method can lower sulphur content of a diesel fuel with sulphur content above 5000 mg/kg to ultra-low specifications. Whilst Case 2 experiments enabled the researcher to determine whether adsorption desulphurisation method employed in series with hydrodesulphurization reactor would lower diesel fuel sulphur content to ultra-low

specifications. The process was conducted under ambient temperature and pressure in a pipex adsorber fitted with a mechanical stirrer. The stirring speed was approximately 120 r/min. Total capacity of adsorber was 250 cm^3 and volume of diesel fuel used was 100 cm^3 per experiment. All experiment variables were kept constant except adsorption time. Varying these experiment variables may be considered for future studies to further optimise the process. On each Case, samples were taken every 10 minutes. On each experiment, a calculated mass of activated carbon was used.

3.4 Analysis techniques

The morphology of the adsorbent was examined using Scanning Electron Microscopy (SEM) techniques. The SEM images were obtained using Scanning Electron Microscopy Zeiss ULTRA 55 model which has a Field Emission Gun (FEG) as the electron source. The sulphur analysis before and after each set of experiments was carried out according to ASTM D5453 standard technique using Fluorescence Spectrometer equipped with energy dispersive X-rays.

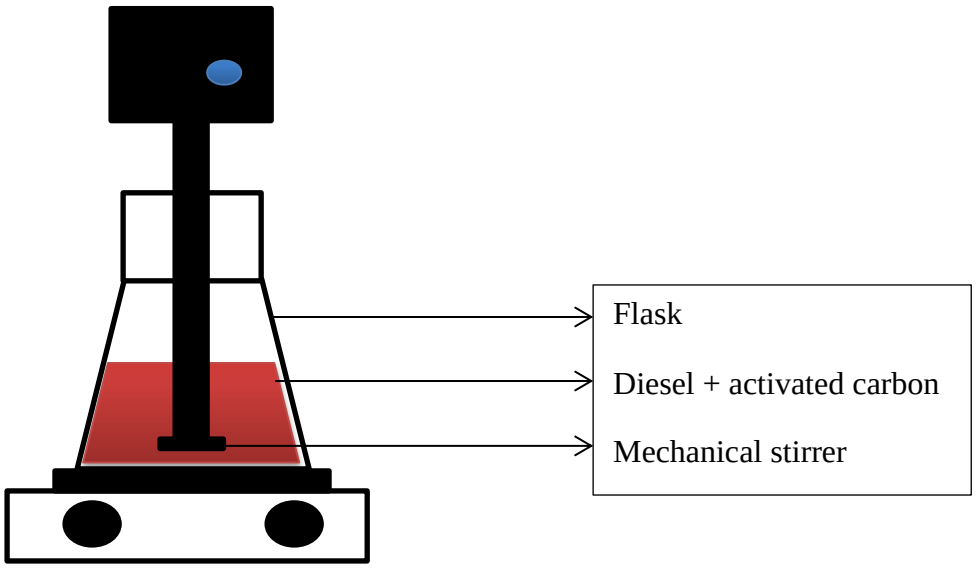


Figure 3.1: Experiment schematic

A hydrocarbon sample was directly injected in a sample boat. The sample was entered into a high temperature combustion tube where the sulphur was oxidised to sulphur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion was removed and the sample was next exposed to ultraviolet light (UV). The SO_2 absorbed the energy from the UV light and was converted to excited SO_2. The fluorescence emitted from the excited SO_2 as it returned to a stable state was detected by a photomultiplier tube. The resulting signal was a measure of the sulphur contained in the sample.

3.5 Chapter summary

The used fuel and activated carbon characteristics were discussed. How the experiment was conducted as well as analysis techniques applied were discussed. The SEM analyses were conducted to understand the activated carbon morphology prior the experiment. The activated carbon surface area was 788.8 $m^2 g^{-1}$. The ASTM D5453 international standard was used to determine the sulphur content on the experiment samples.

Chapter 4: Results and discussion

4.1 Introduction

The aim of this chapter was to discuss the study results obtained from experiment as elaborated in chapter 3. Furthermore, the outcome of the adsorption isotherm and kinetics models were revealed and discussed.

4.2 Case 1 results

In case 1, the initial sulphur concentration, C_0, in diesel was 5200 mg/kg. The sulphur concentration reduced over a period of time as depicted in figure 4.1. The lowest sulphur concentration achieved was 3390 mg/kg. This indicated the incapability of adsorption method to reduce high sulphur content from petroleum distillates to acceptable commercial levels.

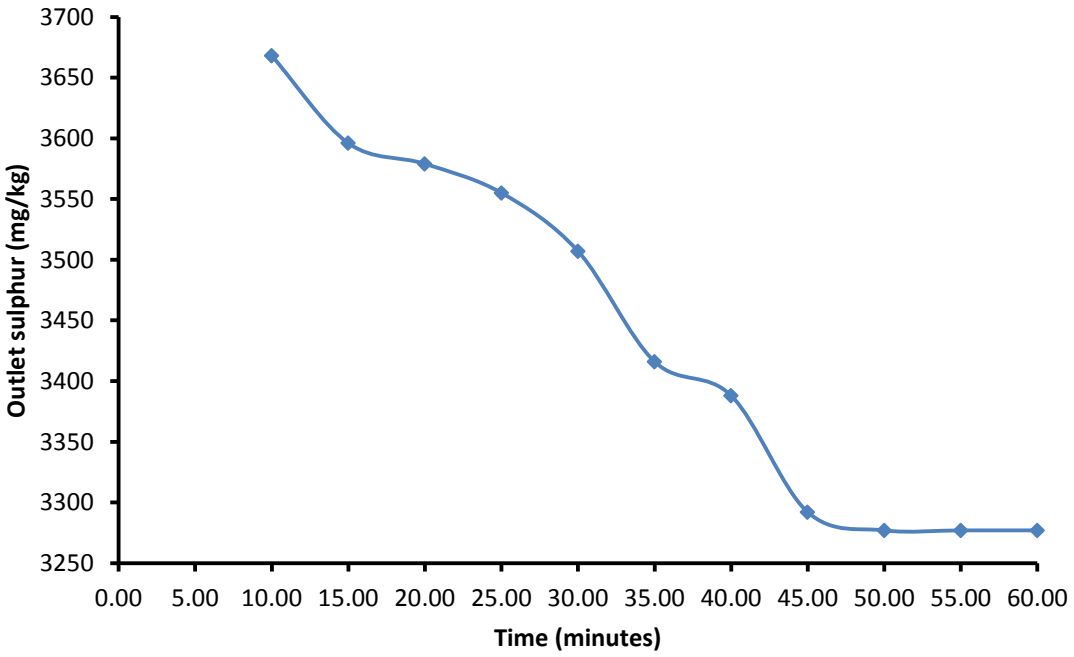


Figure 4.1: Case 1 Outlet sulphur vs adsorption time

The findings supported the literature which states that adsorption desulphurisation method, just like most of desulphurisation methods except hydrodesulphurisation, are not commercially viable. Only 35% of the sulphur was removed from diesel fuel. For a desulphurisation method to be economically viable, it should be able to desulphurised petroleum distillates to acceptable standards at a competitive cost.

The shape of figure 4.1 indicated that equilibrium was completely reached at 46 minutes. The equilibrium point was compared with the calculated using the second-order kinetics and adsorption equations (equation 2i and 2c). The experimental and calculated equilibrium concentrations were 3277 and 3280.8 mg/kg, respectively. Since the two concentrations are very close, it was therefore concluded that the experiment data was a fair representation of the adsorption.

4.3 Case 2 results

In case 2, the initial sulphur concentration in diesel fuel was 120 mg/kg. This was the stream that was already treated by the hydrotreater reactor. The activated carbon managed to reduce the sulphur concentration over a period of time as depicted in figure 4.2. The lowest sulphur content in diesel achieved was 22 mg/kg.

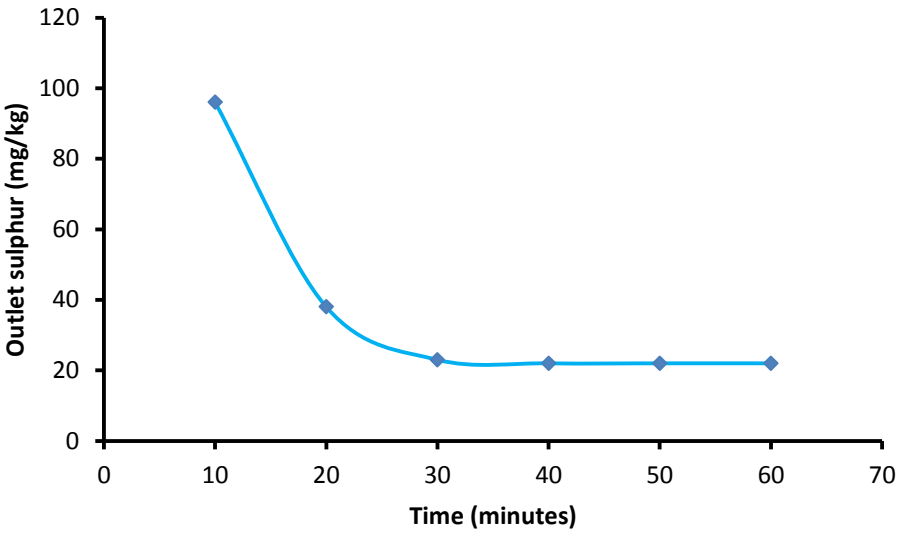


Figure 4.2: Case 2 Outlet sulphur vs time

It was noted that as the sulphur concentration reduced to much lower concentrations, the flatter the curve appeared. This meant that the activated carbon was almost saturated with sulphur thus indicating that not much adsorption was taking place irrespective of adsorption time. This was attributed to the characteristics of the activated carbon used. The findings revealed that 82% of sulphur was removed from the diesel fuel. Therefore adsorption desulphurisation method can be employed in series with the hydrodesulphurisation reactor to achieve commercially acceptable sulphur specifications.

4.4 Adsorption isotherms

Freundlich and Langmuir isotherm models were used to describe the adsorption process. The models were fitted into the experiment data for both case 1 and 2.

4.4.1 Case 1: Hydrodesulphurisation reactor feed

The diesel feed to the hydrotreater reactor had sulphur concentration of 5200 mg/kg. Figure 4.3 exhibits Langmuir adsorption isotherm at the experiment conditions described in section 3.2.

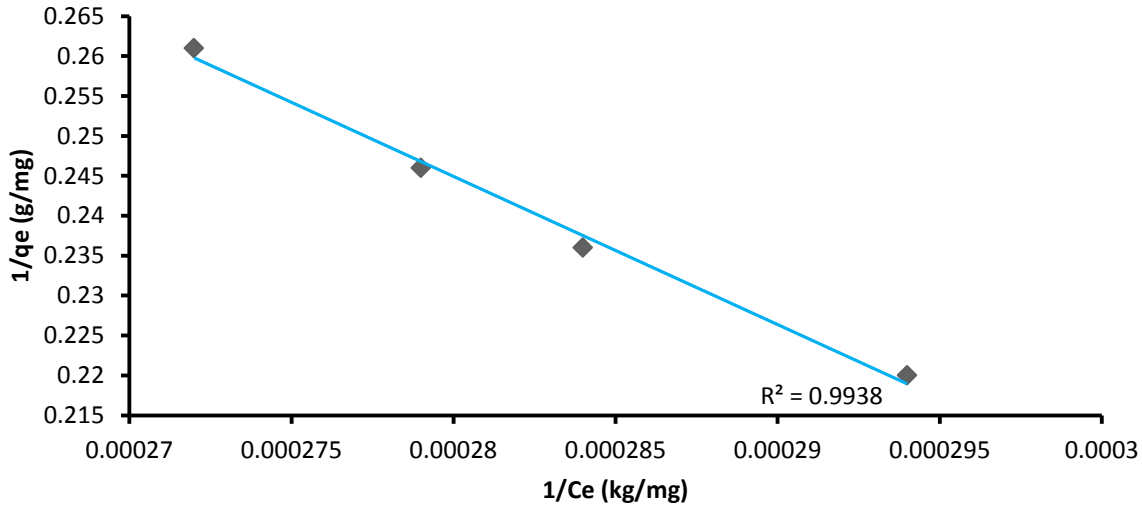


Figure 4.3: Case 1 Langmuir adsorption isotherm

The lowest sulphur composition achieved was *3390mg/kg*. From the figure 4.3, the Langmuir constant, K_L obtained was 1.19 X 10^{-4}. Linear regression was conducted to determine the Langmuir isotherm fit to the experiment data. A regression R^2 of *0.994* was obtained which indicated a good fit.

To examine the progression of adsorption dimensionless constant, separation factor *r* was calculated by following expression (Mittal *et al.*, 2006):

$$r = \frac{1}{1+ K_L C_0} \qquad 4a$$

Where K_L was derived from the Langmuir isotherm and C_0 being the sulphur initial concentration on the diesel fuel. The *r* value indicates the shape of the isotherm to be irreversible *(r=0)*, favourable *(0< r<1)*, linear *(r =1)* or unfavourable *(r>1)* (Lam, 2008).

The calculated *r* was *1.0006*, which was *>1*. Therefore the isotherm was not favourable.

The Freundlich adsorption isotherm model was also applied to describe the adsorption isotherm. Figure 4.4 exhibits the Freundlich isotherm plot.

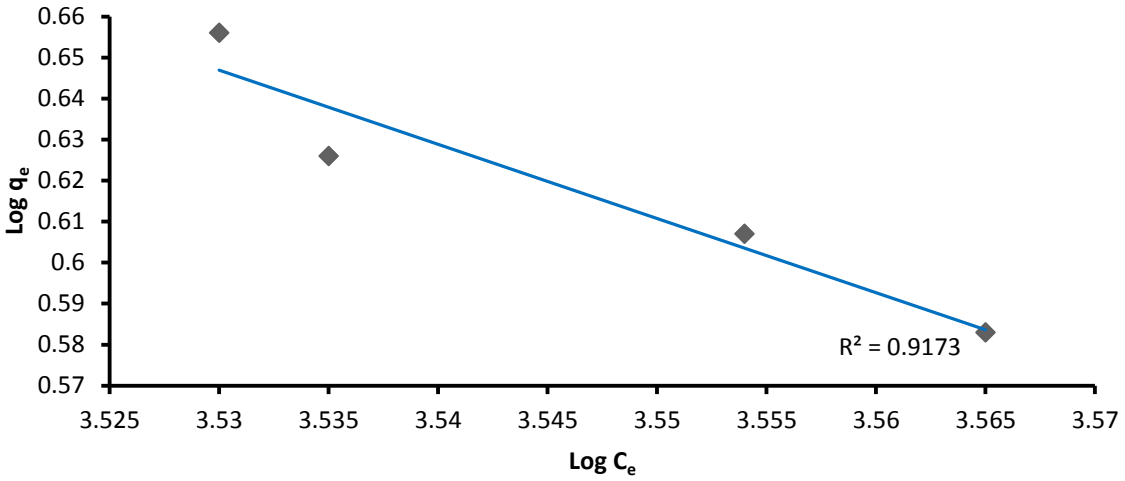


Figure 4.4: Case 1 Freundlich adsorption isotherm

The Freundlich isotherm constants, 1/N and *K*, obtained were *1.807* and *1.05 X* 10^7 respectively. Okeola *et al.*, (2010) suggests that high value of n indicates a strong bond between the adsorbent and the adsorbate. Too strong bond between the adsorbent and the adsorbate is not good for regeneration process. As ease for the adsorbent to be regenerated is one of the key factors in choosing the adsorbent, there is therefore a balance to be maintained between adsorbent and adsorbate bond vs regeneration. The linear regression (R^2) obtained was *0.917* which was lower than 0.95, therefore not indicating a good model fit.

Normally, if the *K* value increase, the adsorption capacity will increase too. The magnitude of *N* gives the favourability of adsorption. The value of $N > 1$, represents favourable adsorption condition (Lam *et al.*, 2008). The obtained *N* from figure 4.4 was *0.553* which did not indicate a favourable adsorption process.

Since Langmuir isotherm model fitted well the experiment data, it can therefore be assumed that there was no interaction between the sulphur molecules during the adsorption process.

Furthermore, all adsorption happened through the same mechanism and the monolayer was formed.

4.4.2 Case 2: Hydrodesulphurisation reactor outlet

The sulphur concentration of the HDS reactor outlet stream was *120 mg/kg* and this was the initial concentration for this adsorption experiment. The lowest sulphur concentration achieved was *22 mg/kg*. Just like the HDS reactor feed experiment, Langmuir and Freundlich adsorption isotherms were applied to model the adsorption experiment equilibrium data. Figure 4.5 depicts the Langmuir adsorption isotherm.

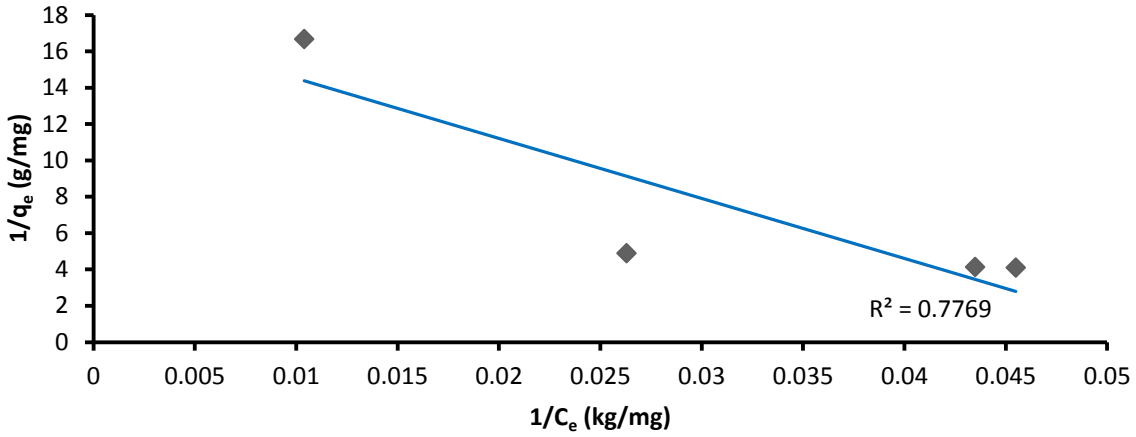


Figure 4.5: Case 2 Langmuir adsorption isotherm

From figure 4.5, the Langmuir adsorption isotherm constant, K_L, obtained was *0.0123 g/mg*. The linear regression *(R^2)* obtained was *0.777* which indicated that the model did not fit the equilibrium experiment data. Also on hydrodesulphurisation reactor outlet set of experiments, separation factor *r* was calculated by following equation 4c. The calculated *r* was 1.0015, which was *>1*. Therefore the isotherm was unfavourable.

The Freundlich adsorption isotherm model was also applied to describe the equilibrium adsorption process. Figure 4.6 shows the Freundlich isotherm.

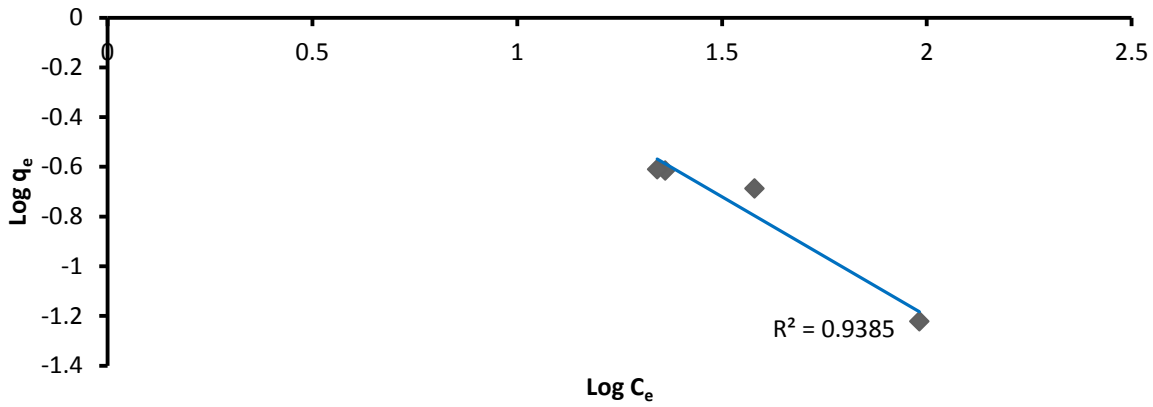


Figure 4.6: Case 2 Freundlich adsorption isotherm

The Freundlich isotherm constants, *1/N* and K_F, obtained were *0.958* and *5.22* respectively. The linear regression *(R^2)* obtained was *0.939* which implied not a good model fit to the equilibrium experiment data. It was noticed that both Langmuir and Freundlich models did not agree with the experiment data which revealed the inapplicability of these isotherm models on the on-going adsorption process. Nonetheless, the Freundlich model fitted better than the Langmuir model. The obtained *N* value from figure 4.6 was *1.04*. This value of n indicated a favourable adsorption process.

4.5 Adsorption kinetics

Kinetics studies were carried out to measure the rates of adsorption under various experimental conditions. Consequently, the kinetic data was processed in order to understand the dynamics of adsorption process in terms of order of rate constant. Appendix C depicts the kinetics data obtained.

4.5.1 Case1: Hydrodesulphurisation reactor feed

The Hydrodesulphurisation reactor feed data were treated with the pseudo-first-order kinetic model (equation 2g) to determine its adsorption process mechanism. Figure 4.7 shows a

linear plot of log (q_e-q_t) versus time plotted. The equilibrium rate constant of the first-order adsorption obtained was *0.0423 min^{-1}*.

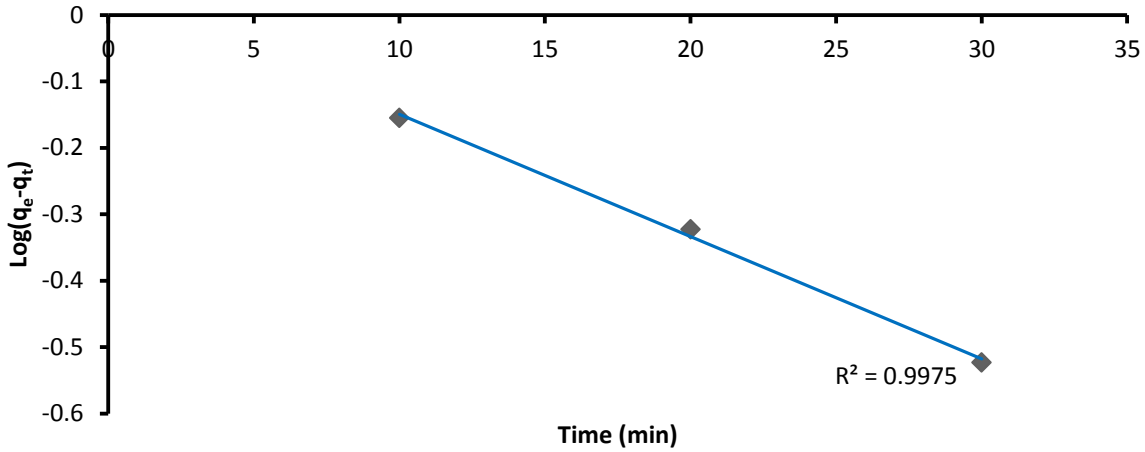


Figure 4.7: Case 1 pseudo-first-order kinetics graph

Figure 4.7 show that the linear regression is *0.998*. The predicted adsorption equilibrium did agree with the experimental value. This therefore meant that the adsorption process did fit the pseudo-first-order model.

To understand the steps of the adsorption process, a plot of B_t vs time was done. Equations 2j and 2k were used to generate the data reflected in table K on the appendix D.

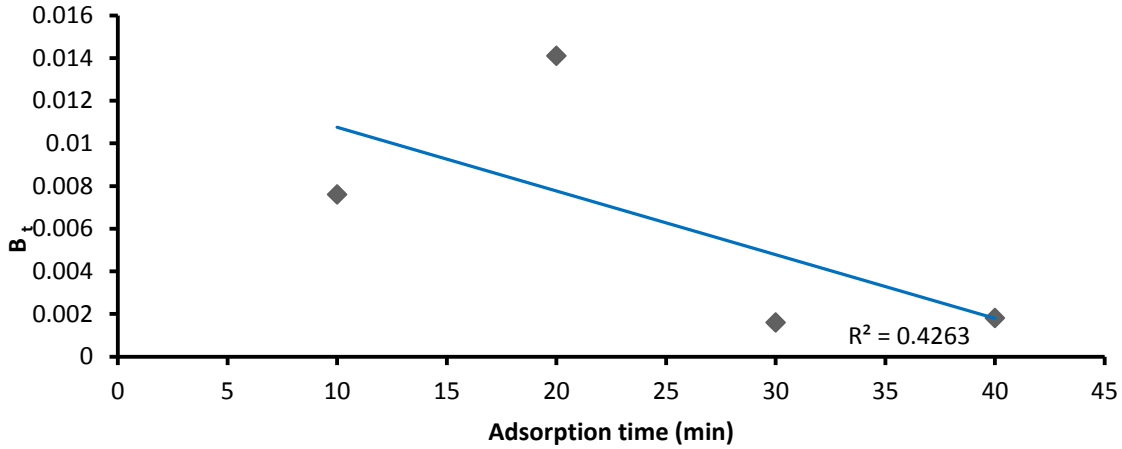


Figure 4.8: Plot of B_t against time for case 1

A plot of B_t against time did not result in a linear shape, therefore the adsorption step taken by the process was particle diffusion which describes the transportation of sulphur within the

pores of the activated carbon except for a small amount of adsorption which occurs on the external surface.

4.5.2 Case2: Hydrodesulphurisation reactor outlet

Just like the HDS reactor feed data, the HDS reactor outlet data were treated with the pseudo-first-order kinetic model (equation 2f) to determine its adsorption process mechanism. Figure 4.9 shows a linear graph of log (q_e-q_t) versus time plotted.

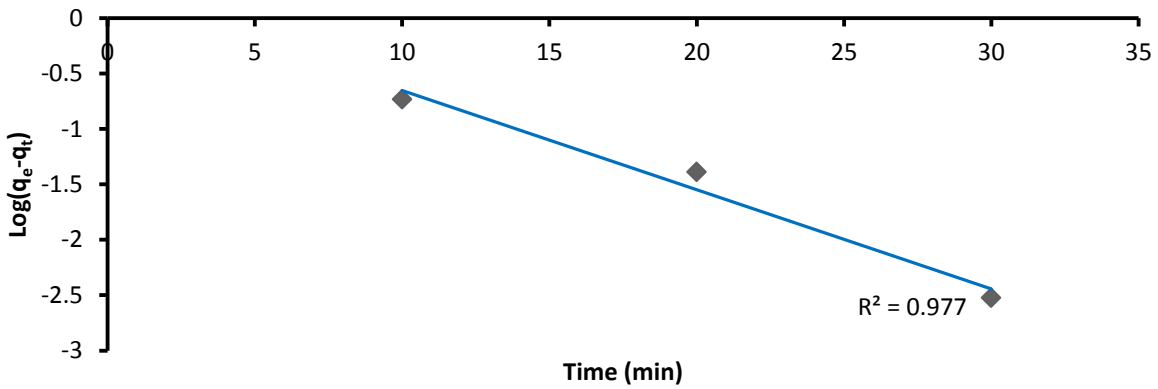


Figure 4.9: Case 2 pseudo-first-order kinetics graph

The equilibrium rate constant of the first-order adsorption obtained was *0.20617 min*$^{-1}$.

Figure 4.9 shows that the linear regression obtained was *0.977* which is above *0.95*. Therefore the adsorption process does fit the pseudo-first-order model.

To further interpret the experiment data, steps in the adsorption process had to be determined. Equations 2j and 2k were used to generate the data reflected in table L in appendix D.

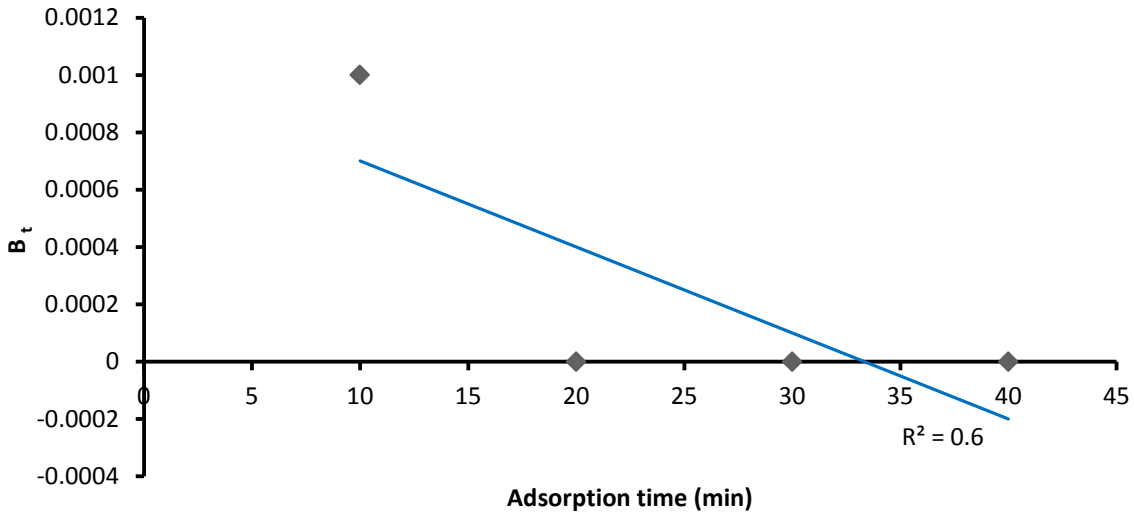


Figure 4.10: Plot of B_t against adsorption time for case 2

The plot of time vs B_t was not linear and not passing through the origin. This means that the sulphur ion was not transported toward the external surface of the adsorbent but within the pores of the activated carbon. Therefore the adsorption of sulphur on the activated carbon was particle diffusion in nature.

4.6 Activated carbon morphology

The coconut shell based activated carbon used in the experiment was examined using scanning electron microscopy (SEM) to determine its surface morphology. Figure 4.11 shows the SEM images taken.

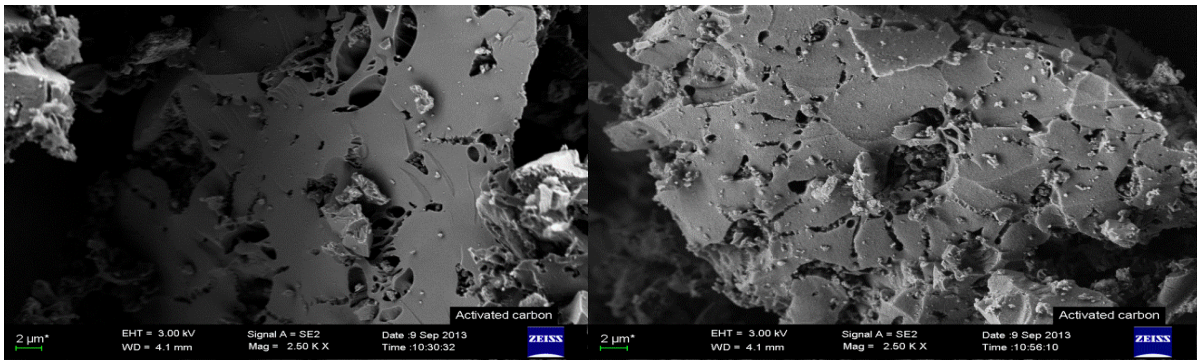


Figure 4.11: Activated carbon SEM images

From these photographs, it was noted that the pore distribution of the activated carbon used was not uniform. As adsorption is a surface phenomenon, uneven distribution of pores has a negative impact on the adsorption capacity. The Aquasorb CP3 activated carbon used had a surface area of 788 m^2/g, which is relatively lower than typical coconut-shell-based activated carbon. This as well had negative impact on the adsorption capability.

4.7 Chapter summary

In Case 1 35% of the sulphur was removed from diesel fuel resulting in 3390 mg/kg sulphur from 5200 mg/kg. This confirmed the outcome from other studies which concluded that adsorption method (irrespective of the adsorbent) cannot effectively remove sulphur from fuels with high concentrations. In Case 2 however, about 82% of sulphur was removed from diesel fuel resulting in 22mg/kg sulphur from 120 mg/kg.

In Case 1, Langmuir adsorption isotherm model fitted the experiment data well (R^2 = 0.994) whereas the Freundlich adsorption isotherm model did not fit the experiment data (R^2 = 0.939). In Case 2 both Langmuir and Freundlich isotherm models did not fit well the data with regression of 0.777 and 0.934 respectively.

Regarding adsorption kinetics: the pseudo-first-order kinetic model fitted the experiment data for both Case 1 and Case 2 with regression of 0.998 and 0.977 respectively. Furthermore, both Case 1 and Case 2 adsorption step taken by the process were particle diffusion in nature. The SEM analysis indicated that the pore distribution of the activated carbon used was not uniform which limited the activated carbon's adsorption capability.

Chapter 5: Conclusions and recommendations

The sulphur concentration of the feed to HDS reactor (Case1) was *5200 mg/kg*. The lowest sulphur concentration that was achieved through adsorption was *3390 mg/kg*. This sulphur concentration is higher than the *10 mg/kg* targeted. The HDS reactor outlet stream (Case2) treated had a sulphur concentration of *120 mg/kg*. The lowest sulphur content achieved through adsorption was *22 mg/kg*. This was also higher than the *10 mg/kg* concentration targeted. The removal of organic sulphur present in petroleum distillates proved to be difficult. However, the use of adsorption desulphurisation method in series with the hydrotreater seems to yield far better results as 82% of sulphur was removed from the diesel fuel. This means these methods combined can reduce petroleum distillates sulphur content from *5200 mg/kg* to only *22 mg/kg*.

There are two major stages in the adsorption process that could be identified as having the biggest influence on the overall adsorption rate, i.e. the change in adsorption capacity with time can be govern by the mass transfer of solute from the liquid to the surface of the adsorbent and the deposition or weak bonding of solute molecules to the surface of the adsorbent (Muzic *et al.*, 2009). However in this experiment, in addition to the above mentioned factors, selectivity of DBT's was the main drive to achieving ultra-low sulphur content.

The micro-pore volume, which has been recognised to have the highest affinity for physical adsorption via dispersive forces, is an important factor in understanding adsorption capacity (Xiong *et al.*, 2011). The coconut shell-based activated carbon used had a pore volume of *0.414* $cm^3\ g^{-1}$. This is relatively lower than other typical activated carbons.

The powdered coconut shell-based activated carbon used had internal diameter between *0.02 –0.250 mm*. Thus it presented a large surface to volume ratio with a small diffusion distance. The micro-pore volume has been recognised to have the highest affinity for physical adsorption via dispersive forces. It is well known that the selectivity is usually the consequence of specific chemical interaction rather than dispersive forces (Xiong *et al.*, 2011), therefore it can be deduced that DBT's selectivity requires chemisorption to achieve ultra-low sulphur content.

Because adsorption is a surface phenomenon, smaller adsorbent particle size tend to offer a comparatively larger and more accessible surface area and hence higher adsorption occurs at equilibrium (Lam *et al.*, (2008). The SEM analysis conducted on the Aquasorb CP3 activated carbon indicated an uneven distribution of pores which affects the adsorption capacity. Therefore the surface morphology of the activated carbon was not uniform. The activated carbon used had a surface area of *788* m^2/g, which is fairly normal for activated carbon but relatively lower than typical coconut shell-based activated carbon. Furthermore, this surface area is smaller than the surface area of the modified activated carbon. In one of his researches, Lam *et al.*, (2008) produced an activated carbon with a surface area of *1091* m^2/g which had more adsorption capabilities. It has been reported that adsorption cannot be generalised, it can only be assessed on a case-by-case bases. Li *et al.*, (2007) conducted an experiment where sulphur adsorption capacity of three different types of adsorbents was studied. He found that the activated carbon with the higher surface area (*906* m^2/g), pore volume *(0.82* cm^3/g*)* and pore diameter *(3.51nm)* had the highest sulphur adsorption efficiency. This further supports the conclusion that the activated carbon used had a relatively lower surface area and pore volume which had a direct impact on the sulphur adsorption.

Ash and fixed carbon content of the activated carbon impact its adsorption capability. Ash is the inorganic, inert, amorphous and unusable part present in the activated carbon. The lower the ash content, the better the activity of the activated carbon. However, the lower the fixed carbon content, the lower the activated carbon activity. The analysed ash content of the used activated carbon was *2.71%* which was within the acceptable range of *2-6%*.

In Case 1, the experimental data could be fitted well into the Langmuir isotherm model due to the correlation coefficients values lie in the acceptable test significance range *(R^2> 0.95)*. This indicated that the homogeneous nature of the activated carbon surface and each sulphur molecule on activated carbon adsorption surface had equal adsorption activation energy. From discussions in section 4.4, it is evident that the adsorption of sulphur onto coconut-shell activated carbon obeyed the pseudo-first-order kinetics and that the overall adsorption rate, in Case 1, was controlled by the chemisorption process. In this model, the rate-limiting step is the surface adsorption where the removal of sulphur from diesel is due to physicochemical interactions between the two phases (Robati *et al.*, 2013). Javadli (2012) proclaims that the application of adsorption to heavy oil, despite its higher sulphur content, is unpractical, due to the poor accessibility of large molecules in the narrow pores and steric hindrance that reduces adsorption effectiveness. This sulphur adsorption on activated carbon phenomenon was the adsorption limiting factor. It has been reported that activated carbon is one of the most important microporous adsorbents due to its incredible adsorptive capacity, an affinity for variety of dissolved organics and ability to be custom-tailored to suit specific application (Ismadji *et al.*, 2005). Modifications of carbon surfaces by incorporation of metals and oxidation of carbon surface can have a positive effect on the adsorption of the DBTs. This happens due to π-electron interactions of sulphur-containing aromatic compounds with metals on the activated carbon and due to oxidation of carbon surface (Srivastava *et al.*, 2011).

Activated carbons with well-developed porous structure and unique surface properties may exhibit good potential as adsorbents for sulphur compounds however their adsorption capacity can be further improved by modification.

According to Xiong (2011), adsorptive desulphurization provides an alternative technology of particular interest due to its low-energy consumption, the practicality of regeneration of spent adsorbent and the ambient operation temperature and pressure. It is presumed that integrating adsorption column system as an upgrade to the existing HDS unit would not be complicated and would not raise the investment and operating costs as much as upgrading the HDS unit itself in order to achieve the desired ultra-low sulphur levels. From the results obtained, it can therefore be concluded that application of adsorption desulphurisation method seem not capable to achieve ultra-low sulphur specification when treating diesel feed with high sulphur content. This was evident in case 1 data. However, the results of the study also revealed that adsorption method can be applied in series with the hydrotreater unit to achieve low sulphur diesel specification.

5.1 Recommendations for future studies

In one of his researches, Xiong *et al.*, (2011) established that cerium-loaded activated carbon had much better adsorption capacity and selectivity towards DBTs than the virgin carbon. This can be prepared by classical soaking impregnation method. This study could be performed using such activated carbons or metal impregnated oxides and zeolite for enhanced adsorption capacity. Furthermore, other regeneration methods can be further investigated to optimise the process from end-to-end.

6. References

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Appendix A: Outlet sulphur analysis data

Table A: Case 1 Outlet sulphur analysis

Time (min)	Outlet sulphur (mg/kg)
10	3668
15	3596
20	3579
25	3555
30	3507
35	3416
40	3388
45	3292
50	3277
55	3277
60	3277

Table B: Case 2 Outlet sulphur analysis

Time (min)	Outlet sulphur (mg/kg)
10	96
20	38
30	23
40	22

Appendix B: Isotherm data

Table C: Isotherm constants

Model	Case 1	Case 2
Langmuir		
K_L (g/mg)	1.19×10^{-4}	0.0123
R^2	0.994	0.777
Freundlich		
K_F	1.05×10^{7}	5.222
1/n	1.8067	0.9587
R^2	0.917	0.939

Table D: Case 1 Langmuir isotherm data

$1/C_e$ (kg/mg)	$1/q_e$ (g/mg)
0.000272	0.261
0.000279	0.246
0.000284	0.236
0.000294	0.22

Table E: Case 1 Freundlich isotherm data

Log C_e	Log q_e
3.565	0.583
3.554	0.607
3.535	0.626
3.53	0.656

Table F: Case 2 Langmuir isotherm data

$1/C_e$ (kg/mg)	$1/q_e$ (g/mg)
0.0104	16.667
0.0263	4.878
0.0435	4.124
0.0455	4.082

Table G: Case 2 Freundlich isotherm data

Log C_e	Log q_e
1.982	-1.222
1.58	-0.688
1.362	-0.615
1.342	-0.611

Appendix C: Kinetics data

Table H: Kinetics constants

Model	Case1	Case2
First-order		
K_{ad} (min^{-1})	0.0423	0.2061
q_e (mg/g)	1.083	1.743
R^2	0.998	0.977

Table I: Case 1 First-order data

Time (min)	log (q_e-q_t)
10	-0.155
20	-0.323
30	-0.523

Table J: Case 2 First-order data

Time (min)	log (q_e-q_t)
10	-0.733
20	-1.39
30	-2.523

Appendix D: *F* and B_t data

Table K: Case 1 *F* and B_t data

***F* values**	**B_t values**
0.03825	0.0076
0.0405	0.0141
0.04225	0.0016
0.04525	0.0018

Table L: Case 2 *F* and B_t data

***F* values**	**B_t values**
0.0006	0.001
0.0021	0
0.0024	0
0.0025	0

Example of Isotherm and Kinetics calculations

Case 1 Freundlich:

$q_e = K_F\, C_e^{1/N}$

In a linear form, equation 2d can be expressed as:

$\log q_e = \log K + \frac{1}{n} \log C_e$

From plot, obtained linear equation: y = -1.8067x+7.024

Therefore 1/n = 1.8067

$\text{Log}K_f$ = 7.024

Case 1 Kinetics:

Legegren's pseudo-first-order equation in linear form: $\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t$

From plot, obtained linear equation: y = -0.0184x+0.0343

Therefore $K_{ad}/2.303 = 0.0184$ and $\text{Log}q_e = 0.0349$