



SIMULATION OF THE ADSORPTIVE DESULPHURISATION OF DIESEL FUEL

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Declaration

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

.....

Signature of F. Sanyangare

..... day of November 2016

Abstract

The global focus on cleaner air has seen sulphur removal processes' gaining popularity and adsorptive desulphurisation has been identified as an effective alternative. Adsorptive desulphurisation was used to simulate and evaluate the performance of the polymer supported imidation agent (Sodium N-chloro-polystyrene sulphonamide) as an adsorbent in the desulphurisation of diesel fuel. This study involved the development of a mathematical model for the adsorption process of sulphur on the polymer supported imidation agent, based on the mass balance on a continuous fixed bed column and pseudo second order kinetics. The developed model was solved using numerical methods, and the simulation of the process carried out varying different parameters; the inlet sulphur concentration, the adsorption column bed height and the particle size (radius) of the adsorbent.

The simulation showed that the adsorption capacity of the studied adsorbent increased with increase in the inlet sulphur concentration; an increase in the adsorption bed height and a decrease in the adsorbent particle size. Validation of the simulation done was carried out by comparing the simulation data with experimental data. The proposed model fit experimental data and can be used to predict the inlet concentration conditions, bed height and particle size of the adsorbent. The overall research enhances the understanding of the adsorptive desulphurisation of diesel fuel using the polymer supported imidation agent and the mathematical modelling of the process.

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List of abbreviations

ADS – Adsorptive Desulphurisation

BDS - Bio-desulphurisation

BT - Benzothiophenes

DBT – Dimethylbenzothiophenes

DMDBT - Dimethyldibenzothiophene

DMF – Dimethylformamide

DMSO - Dimethyl Sulphoxide

EOX - Extractable Organic Halogens

FCC - Fluid Catalytic Cracking

HOMO - Highest Occupied Molecular Orbital

HDS – Hydrodesulphurisation

HSDM – Homogenous Solid Diffusion Model

IL – Ionic Liquids

MATLAB - MATrix LABoratory

MDBT - Methylbenzothiophene

ODS -Oxidation desulphurisation

PDE – Partial Differential Equations

PI – Polymer Supported Imidation agent (Sodium N-chloro-polystyrene sulphonamide)

PSU-SARS - Pennsylvania State University (Selective Adsorption for Sulphur Removal)

S – Sulphur

ULSD – Ultra Low Sulphur Diesel

Chapter 1: Introduction

1.1 Introduction

The global demand for energy has exorably increased over recent years, and is expected to increase by 37% in 2040 at an average growth rate of 1.1% per year (Scenario et al, 2015). Of the available energy sources, oil still remains the primary energy resource with a wide range of possible applications. The current share of world energy from fossil fuels is still over 82%, half of which is from petroleum energy sources. However, the burning of fossil fuels has negative impacts on the environment. This is a result of sulphur contained in various organic and inorganic compounds that are naturally present in fossil fuels. The sulphur emissions cause acid rain which damages buildings, destroys automotive, paint finishes, forests and crops, changes the makeup of soil, ultimately leading to changes in the natural variety of plants and animals in an ecosystem (U.S. EPA, 2005).

Sulphur emissions also cause respiratory illnesses, aggravate heart disease, trigger asthma and contribute to the formation of atmospheric particulates (Gokhale & Khare, 2004). In vehicles, sulphur negatively affects the efficacy of catalytic converters as they strongly adsorb to the precious metal catalysts, preventing the adsorption and reaction of hydrocarbons, nitrogen oxides, and carbon monoxide.

An alternative is the use of clean energy which includes biofuel, solar, wind, and nuclear power to replace fossil fuels. The alternative energy sources however are not fully developed to be used as substantial replacements to fossil fuels. Environmental Protection Agencies and government departments globally have recommended and regulated substantially low sulphur emission limits in fuels (gasoline and diesels) to reduce the impacts from their use.

1.2 Justification

With the increasing stringent restrictions on permissible sulphur emissions, both globally and locally, there is need for oil refineries to reduce the amount of sulphur contained in the refined fuels. The global attention on ultra-low sulphur diesel (ULSD) has seen the introduction of newer emission control technologies, and Europe has taken lead by

introducing a maximum permissible limit of 50 ppm in ultra-low sulphur diesel, since 2005 (EURO 4). Regulations within South Africa require an ultra-low sulphur limit of 500 ppm as of 2006 (Clean Fuels 1), with South Africa's Clean Fuels 2 standard, targeting 10 ppm in 2017 (Manyara & Ikapi-neyer, 2014.). Europe is currently on EURO 5 standard, which limits the ultra-low sulphur in diesel to 10ppm. It is important to note that the force behind the realization of more sulphur removal technologies are the strict specifications for sulphur content in transportation fuels (Rang et al., 2006).

The need for ULSD production in the petroleum refineries is necessitated by environmental problems and health hazards caused by exhaust emissions from the diesel powered engines, the formation of harmful emission components due to sulphur (e.g. particulate matter (PM), NO_x, SO_x and CO), and the environmental legislations on diesel fuel sulphur level and air quality standard as well as the continued increase in the demand of ULSD. The increased unavailability of low sulphur crudes has also necessitated the need for refineries to refine heavier high content sulphur crudes (Mcfarland, 1999).

As can be seen, the global target of zero sulphur emissions in the near future is a great possibility. In addition to catalyst poisoning in both the refining equipment and engine exhaust, sulphur in diesel fuel adds to the production of particulate matter in the engine exhaust which causes health problems, in particular respiratory conditions (SAPIA, 2008). It also reduces the efficiency of the fuel. Achieving ultra-low sulphur diesel limits of 50 ppm or less using the traditional hydrodesulphurisation (HDS) process is difficult due to the presence of refractory sulphur compounds (benzothiophenes, dibenzothiophenes and their alkylated derivatives) which are usually contained in immense amounts in diesel fuel and are inert to hydrotreating (Mužic et al., 2009a; Rang et al., 2006). The application of the conventional HDS process on diesel fuel and fuel oil, has proven ineffective in attaining ultra-deep desulphurisation and would require catalyst volumes of three times more (Rang et al., 2006).

1.3 Scope of the research

To achieve the goal of reducing the sulphur content in fuel to 10 ppm with the current HDS process, using high temperature and pressure, large reactor volume and more active catalyst is indispensable but costly. Therefore, it is essential that a method that can be operated under

moderate conditions with high efficiency in removing sulphur compounds be developed to produce ultra-low sulphur fuels. Various chemical process for thoroughly removing sulphur compounds have been investigated in the past (Gray et al., 2003; Garcia-Ochoa & Gomez, 2004) and adsorptive desulphurisation has been pointed out as one of the effective methods in attaining ultra-low sulphur levels in fuels.

The majority of the research on the adsorptive desulphurisation of transport fuels has been aimed at finding high capacity adsorbents capable of selectively adsorbing aromatic sulphur compounds (Mužic, et al, 2009c). This has mainly been done through laboratory testing of the adsorbents subject to different conditions, involving batch adsorber tests or in small-scale adsorption columns and using model fuels that simulate real fuels. For the current proposed work, industrial diesel fuel will be used. Limited research has been done on the modelling of the adsorptive desulphurisation process itself, with the reference work done by Salem & Hamid, (1997) in an agitated pressure vessel and Mužic et al, (2009a) in a batch adsorption system and in a large fixed bed adsorption column (Mužic et al., 2009a; Mužic et al., 2010 and Mužic et al., 2011).

It is important to note that simulation and computational research are vital for the invention and configuration of improved synthetic adsorbents for the desulphurisation of fuels (Rang et al., 2006) as well as desulphurisation processes. The development of the adsorbents and the preferred process should be guided by the investigation of the kinetics of the desulphurisation processes and design. The research will hence focus on the modelling of the adsorption process of sulphur compounds from diesel fuel and include the kinetics involved. The simulation of the process will also be carried out, and an investigation of the effect of varying some process parameters on the adsorption process.

1.4 Research Aims and Objectives

The aim of this research is to carry out the simulation of the adsorptive desulphurisation of diesel fuel in a fixed bed column using a polymer supported imidation agent (sodium N-chloro-polystyrene sulphonamide) to assess the feasibility of the PI as the adsorbent. To achieve the aim of this research, below are the specific objectives:

- (i) Develop a mathematical model for the adsorptive desulphurisation of diesel fuel in a fixed bed column using a polymer supported imidation agent.
- (ii) Numerically solve the developed model and simulate the adsorption process system for sulphur removal from diesel fuel using MATLAB varying several process parameters; inlet sulphur concentration, bed height and adsorbent particle size.
- (iii) Investigate the performance of the chosen adsorbent based on the proposed model.
- (iv) Validate the simulation results with experimental data.

1.5 Report Layout

The layout of this research is presented below.

Chapter 1: Introduction

The research introduction briefly describes the recent introduced strict regulations on maximum allowable sulphur limits in transport fuels, both within South Africa and globally. A brief summary of adsorptive desulphurisation technology is also given. The introduction also includes the scope of the research, including its aim and objectives.

Chapter 2: Literature Review

The literature review includes:

- (i) A summary of desulphurisation technologies for transport fuels particularly diesel fuel. Adsorptive desulphurisation of diesel fuel is reviewed and previous reports discussed. The choice of the adsorbent is also justified.
- (ii) The kinetic modelling of adsorption processes and various models applicable.
- (iii) A brief summary into the modelling and simulation of adsorption columns.

Chapter 3: Modelling of the adsorptive desulphurisation of diesel fuel

In Chapter Three, a mathematical model for the adsorptive desulphurisation of diesel fuel is developed. The model is solved using numerical methods and simulation of the adsorption process is carried out, investigating the effect of different parameters on the process.

Chapter 4: Simulation of the adsorptive desulphurisation of diesel fuel

The simulation program used is validated and a parametric sensitivity analysis of the program carried out.

Chapter 5: Conclusions and Future Recommendations

Chapter Five gives conclusions on the research and highlights what has been achieved as well as proposing future work.

Chapter 2: Literature review

This chapter will focus on the desulphurisation technologies for transport fuels in particular diesel fuel, process modelling basics and simulation and optimisation using MATLAB.

2.1 Desulphurisation Technologies

Sulphur compounds constitute the critical non-hydrocarbon constituents of petroleum and occur as a variety of components; thiols (mercaptans), sulphides, cyclic sulphides, thiophenes, benzothiophene, dibenzothiophene and naphthabenzothiophene. During the refining process of crude oil, sulphur compounds are concentrated in the residual and other heavy fractions. In addition to catalyst poisoning in both the refining equipment and engine exhaust, sulphur in diesel fuel contributes to the formation of particulate matter in the engine exhaust which causes health problems, in particular respiratory conditions (SAPIA, 2008). It also reduces the efficiency of the fuel. Mercaptans cause the corrosion of copper and brass in the presence of air and also have an adverse effect on the colour stability of gasoline and other liquid fuels (Khalfalla, 2009). Middle fraction distillates from crude oil refining generally contain more sulphur compounds than the higher-boiling fractions.

The desulphurisation of petroleum products is based on two main approaches:

- (i) conventional hydrodesulphurisation (HDS) and
- (ii) non-hydrogen consuming desulphurisation (non-HDS based).

The most abundant form of sulphur in petroleum is from thiophenic elements, constituting 50–95% of total sulphur in crude oil and its fractions. Alkylated derivatives of dibenzothiophene (DBT) are the most common organosulphur compounds typically found in crude oil and fractions used to produce diesel (Mohebbi & Ball, 2008) and DBT and its derivatives have become the model compounds for desulphurisation research.

2.1.1 Conventional Hydrodesulphurisation

Hydrodesulphurisation (HDS) is the most common desulphurisation technique employed currently in most refineries. It is a commercially proven refining process that passes a mixture of heated feed stock and hydrogen over catalysts so as to remove sulphur. The process makes use of molybdenum-based metal sulphide catalysts (normally CoMo/Al₂O₃, NiMo/ Al₂O₃) at high temperatures (typically 200–425 °C) and high hydrogen pressures (150–250 psi) to break the C-S bonds within the molecules and evolve the sulphur molecules as hydrogen sulphide, H₂S see equation 2.1. The evolved gas is then purified and converted to elemental sulphur by the Claus process (Kwak et al, 2000).



Where: a and b represent the number of carbon and the number of hydrogen atoms respectively.

The performance of the process rated on the desulphurisation level, activity and selectivity depends on the properties of specific catalyst used (active species, concentration, support properties, synthesis route), the reaction conditions (sulphiding protocol, temperature, partial pressure of hydrogen and H₂S), nature and concentration of the sulphur compounds present in the feed stream, reactor and process design (Murata et al, 2004). Straight run distillate streams generated from direct distillation of crude oil (such as fluid catalytic cracking (FCC) and hydrocracker units) can easily be desulphurised through hydrotreating by controlling the hydrotreating conditions and making use of appropriate catalysts, to achieve the ultra-low sulphur fuels. However for other streams containing refractory sulphur compounds this is not the case. Several sulphur compounds that have been extensively studied using HDS include thiols, sulphides, thiophene and alkylthiophenes and benzothiophenes (Zhao, 2009). As the number of the rings and methyl substituents increases, the reactivity of the sulphur compounds from mercaptans to alkyl derivated dibenzothiophenes is greatly reduced, see Figure 2.1.

Whilst paraffinic compounds (thiols, thioethers and disulphides) are readily desulphurised, cyclic and especially aromatic sulphur compounds (thiophene or benzothiophene) are less

reactive for HDS and particularly refractory compounds (dibenzothiophene (DBT), methyl dibenzothiophenes (MDBT) and above all 4,6-dibenzothiophene (4,6-DMDBT) and similar multiple alkylated S compounds) are even more difficult to remove (Eßer et al, 2004; Baird et al., 1999). These highly refractory sulphur heterocycles are highly resistant to desulphurisation due to their steric inhibition that precludes the requisite catalyst-substrate interaction (Baird et al., 1999). Recent research in HDS has been directed towards the study of thiophenic compounds because they are the least reactive organosulphur compounds (Zhao, 2009).

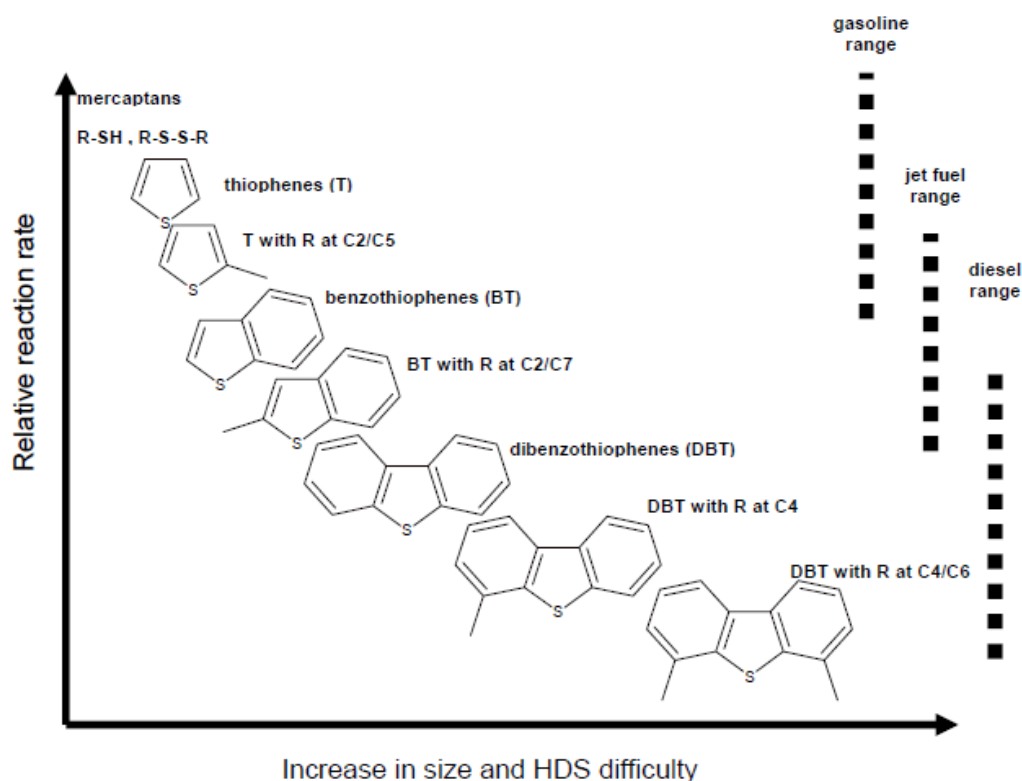


Figure 2.1 Variation of the reactivity with the size of the sulphur containing compounds(Zhao, 2009)

Research on the behaviour of 4,6-alkyldibenzothiophene (4,6-DADBT) has led to different explanations one being the transformation of 4,6-DADBT is limited by the adsorption step via sulphur atom; and the hypothesis suggests that the adsorption occurs through electrons of the aromatic system (Eßer et al., 2004). The removal mechanism of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) through HDS process occurs through two main pathways:

- (i) removal of sulphur without affecting the aromatic rings (direct desulphurisation) through the direct hydrogenolysis of the C-S bonds without prior hydrogenation of either phenyl ring to yield 3,3'-dimethylbiphenyl (3,3'-DMBP),
- (ii) preferential hydrogenation of the aromatic rings of DBT compounds (hydrogenation pathway) resulting in 4H- or 6H-DBT intermediates which are subsequently desulphurised to 3,3'-dimethylcyclohexylbenzene (3,3'-DMCHB) and 3,3'-dimethylbicyclohexane (3,3' DMBCH) by further hydrogenation (Zhao, 2009) see Figure 2.2.

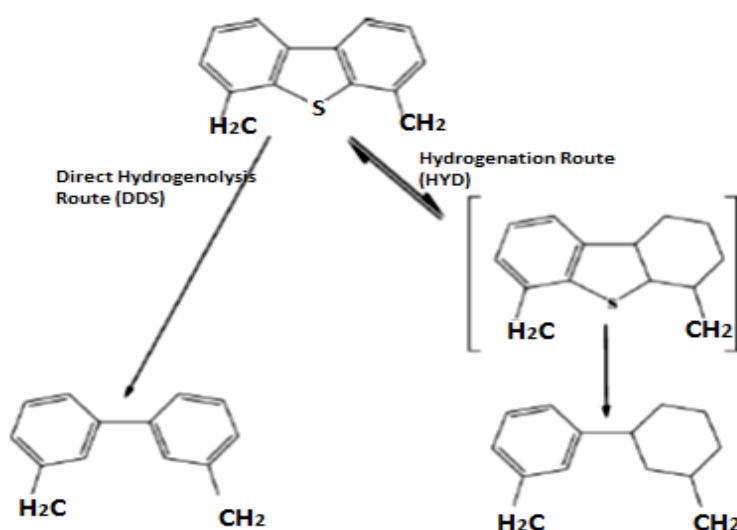


Figure 2.2: Reaction pathways for HDS of alkyl DBT's (Stanislaus et al, 2010)

To achieve the desired ULSD, many factors of the current HDS process such as the catalysts (Fujikawa et al., 2006; Breyse et al., 2008), process parameters (Kim et al., 2006), feedstock source and quality (Marafi et al., 2007; Ho, 2004), reactivities of sulphur compounds, inhibition effects of H₂S (Farag et al., 2003; Leglise et al., 1998), nitrogen compounds (Zeuthen et al., 2001; Ho, 2004) and aromatics (Liu et al., 2008; Song & Ma, 2003) present in the feed, have to be clearly understood as they can have significant influences on the degree of desulphurisation of diesel feeds.

The desulphurisation rate of hindered compounds is greatly increased through the hydrogenation route (Khalfalla, 2009). In the absence of one or both rings, the molecule is much more flexible and the sulphur atom can approach the catalyst surface more easily.

Unconventional benzothiophene and its derivatives have been found to remain in diesel fractions after conventional HDS ranging in concentration between 0.2-0.3 wt% proving that these catalysts are not efficient enough to desulphurise these compounds (Murata et al., 2004). The production of very low levels of sulphur-containing compounds therefore requires the application of severe operating conditions and the use of specially active catalysts (Heeyeon et al., 2003; Khalfalla, 2009) making the process more expensive. Extensive research in the past two decades has been done on developing improved hydrotreating catalysts and processes as well as on finding alternative routes for deep desulphurisation of diesel fuel mainly focused on the effective desulphurisation DBT compounds (Stanislaus et al, 2010).

Intensive efforts have been made to improve the HDS activity of alumina supported CoMo and NiMo catalysts by maximizing the concentration of the type II sites through the use of modified supports, development of new carriers, improvements in catalyst impregnation and preparation techniques, and the use of some additives or modifiers in the catalyst formulation (Stanislaus et al., 2010). Several HDS catalysts improvements have been reported and these include unsupported Ni-W-Mo catalyst with higher thiophene HDS activities prepared by a reflux method, highly active Co/Mo catalyst impregnated with a solution containing Cobalt (Co), Molybdenum (Mo), Phosphorous (P) and nitric acid (HNO_3) on a $\text{HY-Al}_2\text{O}_3$ (Fujikawa et al, 2006); a series of Ni/W catalysts supported on $-\text{Al}_2\text{O}_3\text{-MB-TiO}_2$ denoted as AMBT composites (Wan et al, 2010). These catalysts gave better desulphurisation results over the conventional catalysts with the Ni/W catalysts reaching an HDS efficiency of 99.7% for diesel fuel, and the specifications of the produced diesel oil met the Euro V fuel specifications of ultra-clean diesel.

HDS has several shortcomings in its application for the production of ULSD. The process requires higher temperature, pressure and longer residence time making it more expensive as stronger reaction vessels and facilities will be required (McHale, 1981). For the existing units, which are not competent to meet the new sulphur limits, new HDS facilities and heavy load of capital cost will be required. Revamping the conventional HDS process is essential to achieve ULSD. Although this is not a challenge for the high pressure units which require minor revamp or replacement of catalysts, for the existing intermediate and lower pressure units, significant additional catalyst volume and equipment modifications to increase the hydrogen purity and circulation rate is critical (Gatan et al., 2004). For ULS in fuels, this calls

for the removal of approximately 99.99 % of sulphur from a typical crude containing 1.5 % sulphur which would typically be deep or ultra-deep HDS (Zhao, 2009). Atlas et al., 2001 estimated the cost of lowering the sulphur content from 500 to 200 mg/kg to be approximately one cent per gallon; and to reduce the sulphur content from 200 to 50 mg/kg, the desulphurisation cost would be four times higher, see Table 1 below.

Table 1: Process conditions for ULSD on intermediate and low pressure HDS units (Gatan et al., 2004)

	Intermediate pressure HDS		Low pressure HDS	
	Original	New	Original	New
Sulphur content, ppm	500	<10	500	<10
LHSV, 1/hr	3.0	1.0	1.5	0.5
Gas/Oil Ratio, SCFB	1500	2000	1000	1500
Cycle Length, months	36	18	36	8

The HDS process offers several advantages:

- (i) elimination of nitrogen and metals from organic compounds,
- (ii) induction saturation of at least some carbon–carbon double bonds,
- (iii) removal of substances having an unpleasant smell or colour,
- (iv) clarifying the product by drying it, and
- (v) improval the cracking characteristics of the material (McFarland, 1999; Monticello, 2000; Swaty, 2005).

A proposed enhancement on the HDS process is the utilization of two-stage process. Conventional catalysts, such as CoMo/Al₂O₃ or NiMo/Al₂O₃, can be used in the first stage; whereas, and types of sulphur resistant noble metal/zeolite catalysts are employed in the second stage (Darwish, 2015). Another improvement in the utilization of HDS is the improvement of the SK–HDS process which has an additional adsorptive desulphurisation step prior to the HDS process in order to remove the nitrogen based polar compounds which allows for the reduction of the sulphur to ultra-low levels. For ULSD, a two-stage deep desulphurisation process is required. The first stage could be a conventional hydrotreating unit with moderate processing and the second stage could employ substantial modification of

the desulphurisation process, primarily through use of higher pressure, increasing hydrogen flow rate and purity, reducing space velocity, and choice of the catalyst.

Most hydrodesulphurisation units consist of a fixed-bed, down-flow reactor. A typical HDS plant consists of a reactor, high pressure separator and a stripper, see Figure 2.3 below. Hydrogen is used in excess and is often recirculated after H_2S scrubbing. A major challenge for the sustainable application of the HDS process is to continually decrease the sulphur content while maintaining the quality of fuels by employing more selective catalysts. The need to desulphurise the cracked stocks in addition to the straight-run streams will direct the refiners to choose the most cost-effective technology (Khalfalla, 2009). Alternative processes without the need for high pressure and hydrogen are therefore of high interest for refiners Seeberger & Jess, 2010.

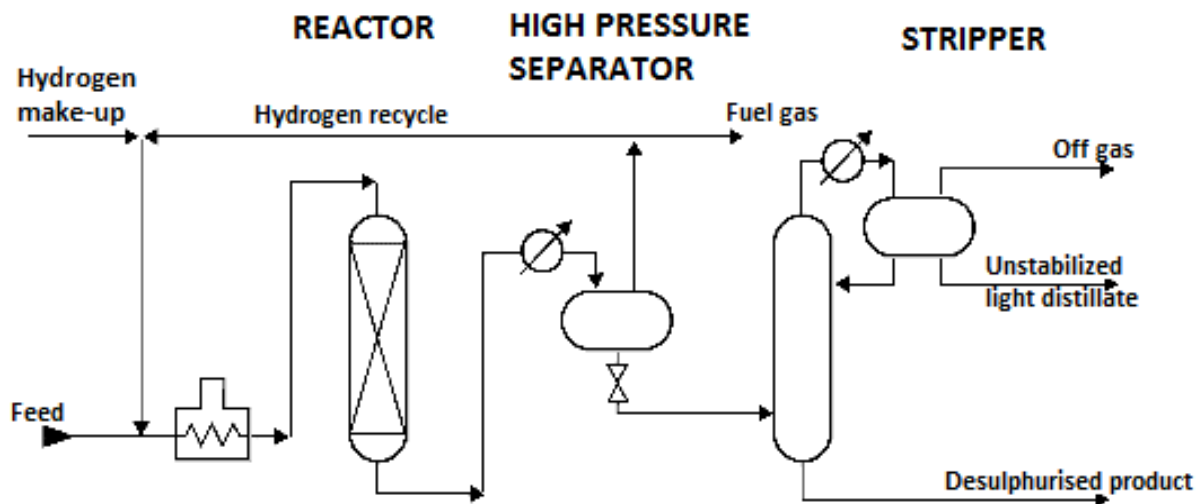


Figure 2.3: Schematic of distillate hydrodesulphurisation (SET Laboratories, 2016)

2.1.2 Non- Hydrodesulphurisation based

Major advances in research has focused on developing new alternatives processes to the conventional catalytic HDS process in attaining ultra-low sulphur levels in fuels. Non-HDS technologies do not use hydrogen for the catalytic decomposition of organic-sulphur compounds and do not require high temperatures and pressures as well as the more active catalysts. In addition to increase the effectiveness of the HDS process longer residence times and additional reactor volumes are required. It is in this light that research has also been done

on the possibilities of developing new processes for desulphurisation, particularly aimed at removing highly refractory sterically hindered S-compounds under mild operating conditions. Among these, oxidative desulphurisation (ODS), biodesulphurisation (BDS), adsorptive desulphurisation (ADS) and S-extraction using solvents and ionic liquids have been investigated, as well as other interesting new technologies.

2.1.2.1 Shifting the Boiling Point by Alkylation

This process involves the shifting of the boiling temperature of organic-sulphur compounds to a higher value, and the compounds are removed from lighter fraction and concentrated in the heavy boiling part of the refinery streams (Khalfalla, 2009; Pawelec et al, 2012). British Petroleum (BP) applied this technology in the desulphurisation of FCC gasoline streams by Olefinic Alkylation of Thiophenic Sulphur (OATS). The alkylation of thiophenic compounds occurs through a reaction between the alkylation agent (alcohols and alkenes (Pawelec et al., 2012; Alexander et al, 2000)) and the olefins in the stream in the presence of alkylation catalysts (BF_3 , AlCl_3 , ZnCl_2 or SbCl_5 , phosphoric acid, H β zeolite and mesoporous materials (Pawelec et al., 2012; Alexander et al, 2000; Zhang et al, 2007)) resulting in a sulphur containing alkylate with a much higher temperature. Separation is then done by distillation. The higher boiling compounds produced can be blended into the diesel pool and hydrotreated.

The OATS process consists of a pre-treatment section, an OATS reactor, and a product separation unit, conventional distillation column (Figure 2.4). Desulphurisation levels of over 99.5% have been reported in gasoline streams. The OATS process also consumes less hydrogen as compared to the HDS process. A major disadvantage of the OATS process is that the alkylated sulphur compounds produced require more severe hydrotreating conditions to eliminate sulphur (Pawelec et al., 2012). While there is need to improve the activities of the catalysts to improve the process, another major challenge with this technology is the need to prevent alkene oligomerization and aromatics alkylation occurring together (Pawelec et al., 2012). These reactions occurring together decrease the efficiency of the process and reduce the gasoline yield. Variation in the catalyst acidity could lead to a change in the activity of the thiophenic alkylation, alkene oligomerization and aromatics alkylation (Pawelec et al., 2012).

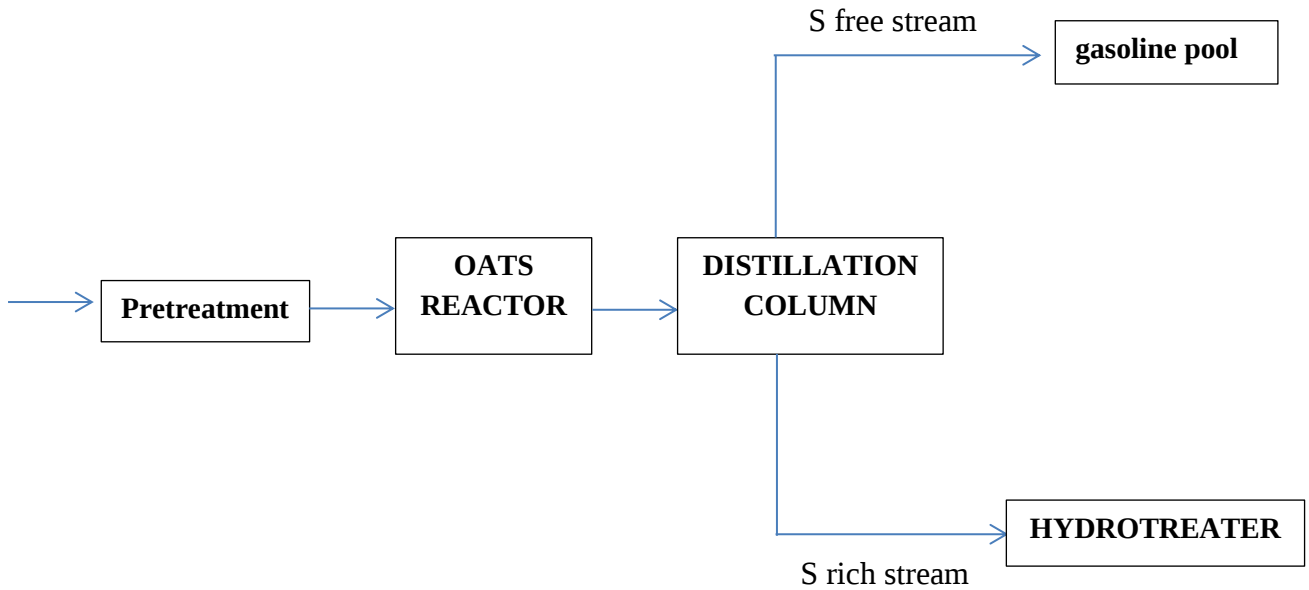
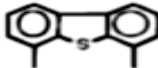
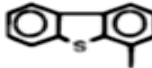
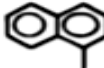
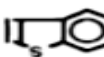
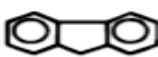


Figure 2.4: OATS Process (Babich & Moulijn, 2003)

2.1.2.2 Desulphurisation by Precipitation (via Charge Transfer Complex Formation)

Refractory sulphur compounds have an electron-rich structure (Milenkovic et al., 1999) and hence have a high potential of forming insoluble charge transfer complexes (CTCs) between the electrons in the sulphur species and π -electron acceptors. Desulphurisation by charge transfer complex formation is based on the formation and subsequent removal of insoluble charge-transfer complexes formed between suitable π -acceptors and alkylated dibenzothiophenes. CTCs are a promising option for desulphurisation due to their high electron density. Being insoluble in the organic phase, on complex formation with the sulphur species, the organic sulphur compounds precipitate out of solution and can be easily removed (Milenkovic et al., 1999). The complexing abilities of dibenzothiophenic compounds can be classified by determining their oxidation potentials and calculating their HOMO (highest occupied molecular orbital) (Milenkovic et al., 1999). The higher the HOMO, the lower the oxidation potential and the stronger the association with π -acceptors, see Table 2 with typical values.

Table 2: Experimental and Theoretical Approach to the Determination of the Ability of Aromatic Compounds to Form CTC (Milenkovic et al., 1999)

	Aromatic compound	EOX (V/SCE)	HOMO (eV)
	2,8-DMDBT	1.44	-8.44
	4,6-DMDBT	1.53	-8.51
	4-MDBT	1.57	-8.55
	DBT	1.60	-8.60
	MN	1.63	-8.71
	Benzothiophene	1.70	-8.80
	Fluorene	1.79	-8.84

Milenkovic et al., (1999) showed that 2,4,5,7-tetranitro-9-fluorenone (TNF) as the most promising complexing agent, with approximately 15% sulphur removal in 860 ppm and 1130ppm model gas oils. Koltai et al., (2002) investigated the effect of pretreating HDS with complexing agents before the HDS process, and reported improved desulphurisation efficiencies. The CTC formation enhanced desulphurisation of the refractory species, increased the rate of desulphurisation, particularly at deep HDS conditions (i.e. lower sulphur concentrations). Macaud et al, (2004) investigated the effect of selective nitrogen compounds removal on gas oil deep desulphurisation. It was found that the HDS performance was greatly enhanced by preliminary denitrogenation of feed by a combination of charge transfer and ion exchange processes.

Meille et al, (1998) investigated the desulphurisation of model 4,6-DMDBT (dimethyldibenzothiophene) in 1-MN(methylnaphthalene) and heptane with a π acceptor (tetranitrofluorenone (TNF) gave the best results). They went on to model gas oil (960ppm) and pure gas oil (1920ppm) in heptane using TNT and 60wt% sulphur removal was reported. From the reported literature the desulphurisation efficiency is low. More research needs to be conducted on creating polymers containing π -acceptor structures (and which are easily

regenerated) and on new processes for limiting the sulphur level in the gas oil by formation and subsequent removal of charge-transfer complexes (Meille et al., 1998). The use of a solid or inorganic complexing agent may simplify the process as the filtration and π -acceptor steps are avoided (Babich & Moulijn, 2003). Specific elimination of dibenzothiophenic compounds by CTC could be performed before hydrotreatment; such pretreatment may allow the catalytic process to be run under milder conditions (Koltai et al., 2002). Research on the synthesis of materials (insertion of the δ -acceptor by covalent bonding into organic or inorganic matrix) is now also being carried out.

2.1.2.3 Photochemical desulphurisation

Photochemical desulphurisation is the process by which polar organo-sulphur compounds are removed from fuels using liquid extraction with a polar solvent (water, acetonitrile), followed by photochemical oxidation in the solvent phase (Shiraishi et al, 1999) resulting in the accumulation of sulfoxides and sulphones in the polar phase. Most of the research in this area was reported in the late 1990's (Hirai et al, 1996; Shiraishi et al, 1998; Shiraishi et al., 1999) and not much literature has been found afterwards.

Hirai et al, (1996) investigated the desulphurisation of DBTs by photochemical reaction (UV irradiated by immersing a high-pressure mercury lamp) in combination with liquid-liquid extraction. The DBT compounds were photodecomposed by UV light in the organic phase and the resulting sulphur compounds removed into the water phase as SO_4^{2-} . The desulphurisation was facilitated by the supply of O_2 by air bubbling and the reactivity of the DBTs was reported to be in the order of $\text{DBT} < 4\text{-MDBT} < 4,6\text{-DMDBT}$, which is different from the order typically reported in HDS process. On application of the process to the desulphurisation commercial light oil only 22% of sulphur was removed after 30 hrs of irradiation.

The deep desulphurisation of light oil by a combination of photochemical reaction and organic two-phase liquid-liquid extraction was investigated and the sulphur content of commercial light oil was reported to have been reduced from 0.2 to 0.05 wt % after 2 h of irradiation and that of light gas oil from 1.4 to 0.05 wt % after 10 h of irradiation (Shiraishi et al., 1998). Hirai et al, (1997) investigated the effect of adding a photosensitizer and hydrogen

peroxide in the desulphurisation of light oil by photochemical reaction and liquid-liquid extraction. The addition of benzophenone (BZP), a triplet photosensitizer, enhanced the removal of DBT from tetradecane and the addition of hydrogen peroxide enhanced the desulphurisation of commercial light oil as well as the removal of DBT from tetradecane. The desulphurisation yield of commercial light oil was 75% after 24 hours of photo-irradiation and the sulphur content in the light oil was reduced from 0.2 wt % to less than 0.05 wt % (Hirai et al., 1997).

The application of photochemical techniques for the desulphurisation of fuel oils if proven feasible for commercial application offers a number of advantages over the conventional HDS process. No catalysts are required for the process, it is easy to operate and to control the reaction, the reaction occurs at room temperature and under atmospheric pressure and the deep desulphurisation of refractory sulphur compounds such as 4-MDBT and 4,6-DMDBT as well as DBT may be feasible (Hirai et al, 1996).

2.1.2.4 Extractive Desulphurisation

The separation of sulphur compounds from fuel oil by extraction (extractive desulphurisation) is based on the fact that sulphur compounds are more soluble than hydrocarbons in appropriate selective solvents (Pawelec et al., 2012) . It is a liquid-liquid extraction process and the two liquid phases must be immiscible. The diesel stream to be desulphurised is contacted with the solvent and mixed in a tank where the sulphur compounds are transferred from the oil phase into the solvent due to their higher solubility in the solvent. The solvent–fuel mixture is then separated by distillation and the desulphurised oil is separated from the solvent. The solvent can be recycled. There are two main processes for extractive desulphurisation, conventional extractive desulphurisation and extraction using ionic liquids.

2.1.2.4.1 Conventional extractive desulphurisation

Conventional solvent extraction technique has been utilized for the removal of sulphur compounds from petroleum feeds based on the solvent's polarity. The feedstock is mixed with the solvent and the organosulphur compounds are extracted into the solvent due to their higher solubility in the solvent. The mixture is then separated by distillation and the

hydrocarbon is separated from the solvent. The treated hydrocarbon can be further processed and the recovered solvent recycled to the mixing tank. Figure 2.5 below shows a typical process flow for the process. Several solvents have been examined for the removal of sulphur compounds, such as acetone, carbon disulphide, ethanol, dimethyl sulphoxide (DMSO), DMF, n-butyl alcohol, methanol, lactones (i.e., gamma butyrolactone), N-containing solvents and water (Moosavi et al, 2012; Pawelec et al., 2012; Funakoshi & Aida, 1998; Forte, 1996) and polyethylene glycols (Forte, 1996).

Different types of solvents examined showed 50–90% desulphurisation rates depending on the number of extraction cycles of the process (Funakoshi & Aida, 1998; Forte, 1996; Javadli & Klerk, 2012). Sulphur removal of sevenfold magnitude for a hydrotreated middle distillate from 0.2% to 0.029% S content and a threefold for aromatics from 27.1% to 8% S content by extraction with solvents such as methanol, furfural and ethylene glycol has been reported (Pawelec et al., 2012). In addition to solvent polarity several other factors that may affect the separation and recovery of the solvent need to be considered and these include the melting point, the boiling point and the surface tension. The process is however characterized by a poor sulphur removal capacity attributed to the slight difference of the polarity between the contained sulphur compounds and the aromatic hydrocarbons.

Toteva et al, (2007) proposed a two-stage extraction process with dimethylformamide as a solvent for the desulphurisation of diesel fuel, see Figure 2.5. Sulphur content removal from 2.0 wt. % to around 0.33 wt. % was reported. The polarity and solubility of the sulphur compounds in the solvent can be improved by oxidizing the sulphur compounds before employing the extraction step to attain ultra-low sulphur content. Zannikos & Lois, (1995) reported desulphurisation rates of up to 90% using oxidation and consequently solvent extraction for the desulphurisation of gas oil. Modified extractive desulphurisation processes have been proposed – UniPure aromatic sulphur reduction technology and SulphCo desulphurisation technology. UniPure process is different from the conventional extractive desulphurisation process in that an aqueous phase is applied along with the oxidative catalyst (Babich & Moulijn, 2003). The process has been reported to reduce S from 270ppm to 2ppm at atmospheric pressure and mild temperatures. SulpCo desulphurisation process applies ultrasound energy to oxidise sulphur compounds in a water-fuel emulsion containing H_2O_2 (Babich & Moulijn, 2003).

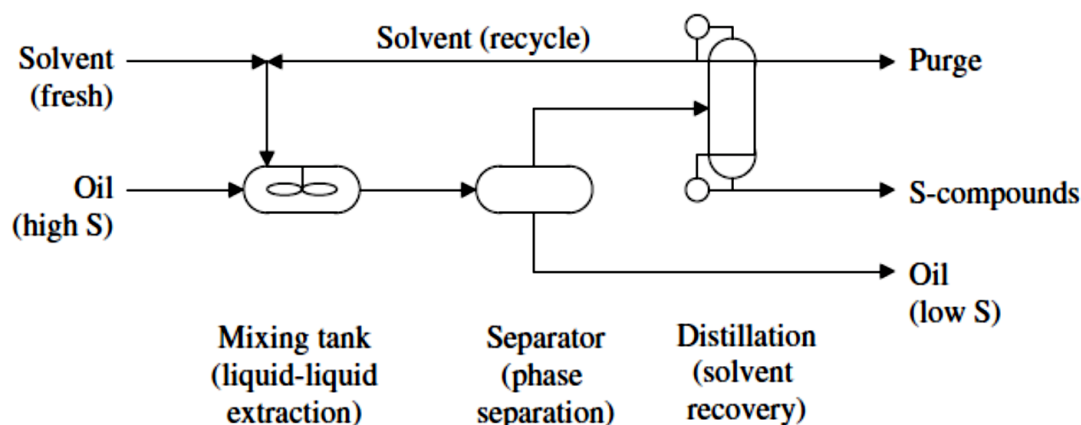


Figure 2.5: Process flow for extractive desulphurisation (Khalfalla, 2009)

Extractive desulphurisation is an attractive option for the desulphurisation of fuels as it is a straightforward industrial application, does not require hydrogen, and can be operated under moderate process conditions and the mixing tank can be operated at near-ambient conditions. As the efficiency of process is limited by the solubility of the organosulphur compounds in the solvent the need to select the appropriate solvent is very important for efficient desulphurisation. Solubility can be enhanced by preparing mixture of two or more solvents or by transforming the organosulphur compounds to increase their polarity e.g. by oxidising the organosulphur compounds to sulphones. The need to make use of a light solvent and the potential loss of solvent by dissolution in such a complex matrix as heavy oil erodes the cost effectiveness of extractive processes for desulphurisation of heavy oil (Javadli & Klerk, 2012).

Solubility can be enhanced by selecting an appropriate solvent taking into account the nature of the sulphur compounds to be removed. This is usually achieved by preparing a ‘solvent cocktail’ such as acetone–ethanol or a tetraethylene glycol–methoxytriglycol mixture. Preparation of such a ‘solvent cocktail’ is rather difficult and intrinsically non-efficient since its composition depends strongly on the spectrum of the organic sulphur compounds present in the feed stream. The most attractive feature of the extractive desulphurisation is the applicability at low temperature and low pressure. The process does not change the chemical structure of fuel oil components. To make the separation of the process efficient, the solvent must be carefully chosen to satisfy a number of requirements. The sulphur compounds must be highly soluble in the solvent. The solvent must have a boiling point different than that of

the sulphur containing compounds, and it must be inexpensive to ensure economic feasibility of the process.

2.1.2.4.2 Extraction using ionic liquids

Ionic liquids (ILs) have been suggested as a potential option for the desulphurisation of transport fuels by extraction. ILs are widely applied in liquid-liquid extraction processes due to their flexibility in modulating their hydrophobic or hydrophilic nature by modifying the cations and anions. ILs have been used in chemical industries, pharmaceuticals, algae processing, gas separation, nuclear fuel reprocessing, solar thermal energy, waste recycling and fuel desulphurisation (Darwish, 2015). ILs such as tetrafluoroborate, chloroaluminate and hexafluorophosphate are, are efficient in the extraction of DBT derivatives contained in diesel oil (Brennecke & Maginn, 2001). However, explaining variations in the extraction of DBT by different ionic liquids is difficult as factors such as the size, shape, aromaticity and charge distribution play important roles (Holbrey et al., 2008).

ILs containing CuCl_2^- , Cu_2Cl_3^- and Cu_3Cl_4^- anions, resistant to moisture and air, have been used for the desulphurisation of a model fuel and they showed a high ability to desulphurise gasoline (Huang et al, 2004). From the first published literature, chloroaluminate ionic liquids were used for the desulphurisation of diesel fuel and 80% sulphur removal was reported using a five-stage-extraction process operated at a temperature of 60 °C (Bosmann et al., 2001). However, the process showed some hydrolytic instability, which makes application of the process difficult. Nie et al, (2006) studied the feasibility of imidazolium-based phosphoric ILs (*N*-methyl-*N*-methylimidazolium dimethyl phosphate ([MMIM][DMP]); *N*-ethyl-*N*-methylimidazolium diethyl phosphate ([EMIM][DEP]) and *N*-butyl-*N*-methylimidazolium dibutyl phosphate (BMIM)[DBP]) in the desulphurisation of gasoline. The study reported the desulphurisation capability of the ILs to be in the order of [BMIM][DBP] > [EMIM][DEP] > [MMIM][DMP] and the sulphur removal selectivity for S-compounds in the order of DBT > BT > 3-MT. Holbrey et al., (2008) investigated several ionic liquids with different cation classes (pyridinium and pyrrolidinium) and a set of anion classes for liquid-liquid extraction of DBT and dodecane and reported the partition ratio of DBT to the IL to show a clear variation with cation class when compared to the variation with anion class and reported the highest extraction potential using polyaromaticquinolinium-based ionic liquids.

It was also shown that there is a direct proportionality between the absorption capacity of ILs and the number of alkyl groups (Thomas, 2008). Results showed that using different ILs based on 3-methylimidazolium (MIM) such as 1-alkyl 3-methylimidazolium (AMIM), butyl 3-methylimidazolium (BMIM) and ethyl 3-methylimidazolium (EMIM), increased the absorption capacity of thiophene to higher than that of 2-methylthiophene. Advances in liquid-liquid extraction technologies involve combining oxidative desulphurisation and ILs extraction (Zhang et al., 2009). This results in 96.1% sulphur removal from DBT model diesel oil which is much higher than for conventional solvent extraction or oxidative desulphurisation. For extraction using ILs, desulphurisation levels of 50–90% have been reported for different extraction cycles (Darwish, 2015). Ionic liquids can be regenerated by treating the extract with an excess of low boiling paraffins (Pawelec et al., 2012). However this process is not efficient owing to the significantly low vapour pressure of the sulphur compounds extracted and contained in the IL.

Currently the application of extractive desulphurisation using ionic liquids has only been limited to academic interest for desulphurisation, much like biodesulphurisation methods. Although ideal ionic liquids have high distribution coefficients for sulphur compounds, low cross solubility for hydrocarbons, low viscosity and fast phase separation rate after mixing and extraction, the performance of real ionic liquids for liquid–liquid extraction is less favourable (Javadli & Klerk, 2012). The efficiency of ionic liquids extraction processes can be increased by oxidising the organo-sulphur compounds to increase the distribution coefficient, before extraction. As ILs are high boiling solvents, recovery of extracted sulphur compounds is more challenging than with organic solvents (Javadli & Klerk, 2012). Several approaches were proposed for the extraction of the sulphur compounds and these include distillation; extraction with a low boiling point solvent; and addition of water to reduce the distribution coefficient of the sulphur compounds and ultimately evaporating the water (Seeberger & Jess, 2010; Huang et al., 2004; Bosmann et al., 2001).

Extractive desulphurisation using ionic liquids shares most of the advantages as previously stated for conventional extractive desulphurisation with organic solvents. Limitations on the exploration of ionic liquids in industrial application are mainly due to their high cost and water sensitivity. It is also important to note that ionic liquid extraction is not feasible for the desulphurisation for heavy oil.

2.1.2.5 Oxidative Desulphurisation (ODS)

Oxidative desulphurisation is based on the selective removal of sulphur compounds by oxidation owing to the fact that oxidised sulphur compounds such as sulphones or sulfoxides are substantially more polar than unoxidised sulphur compounds, and can be subsequently removed by solvent extraction or solid adsorption is feasible (Yazu et al, 2001; Shiraishi, et al, 2003; Khalfalla, 2009). Two steps are involved; the oxidation step and the sulphur removal step (typically by liquid extraction) step. Several oxidants have been successfully applied in the desulphurisation of fuels and these include organic peroxides, hydroperoxides, nitrogen oxides, peroxy salts and ozone (Pawelec et al., 2012), t-butyl hypochlorite, ozone and t-butyl hydro-peroxide (Darwish, 2015) and more recently polyoxoperoxo complexes (Mei et al., 2003). To improve the oxidation reaction both homogenous catalysts (e.g. organic acids, polyoxometallic acids and their salts in aqueous solution) and heterogeneous catalysts (e.g. transition metal compounds such as Mo/Al₂O₃, Co/Mn, Ti-silica, Ti-MCM- (Zhou et al., 2009), modified active carbons (Yu et al, 2005), vanadosilicate molecular sieves (Shiraishi et al, 2003) and supported-transition metal oxides have been used. Hydrogen peroxide and transition metal catalysts have proven to be the best catalysts for the oxidation of the sulphur compounds (Pawelec et al., 2012).

On contacting of the oil with the oxidant, oxidized S-containing compounds are formed. The used oxidant can be regenerated. The oxidized compounds are extracted from the oil by solvent extraction with a non-miscible solvent (acetonitrile, DMF and DMSO), selective for the relatively polar-oxidized S-containing compounds. Acetonitrile is particularly suitable due to its relatively low boiling temperature (82 °C) and its easy separation from the sulphones (Pawelec et al., 2012). When acetonitrile is contacted with light oil, a large quantity of aromatics is extracted simultaneously with the sulphones. The addition of water, however, suppresses the extraction of the sulphones. The freezing point and the surface tension should also be considered in the selection of the solvent. The oxidized compounds and solvent are then separated from the oil by decantation, whereas the solvent is separated from the mixture of solvent and oxidized compounds by a simple distillation for recycling. The solvent is separated from the mixture by distillation, for recycling, see Figure 2.6.

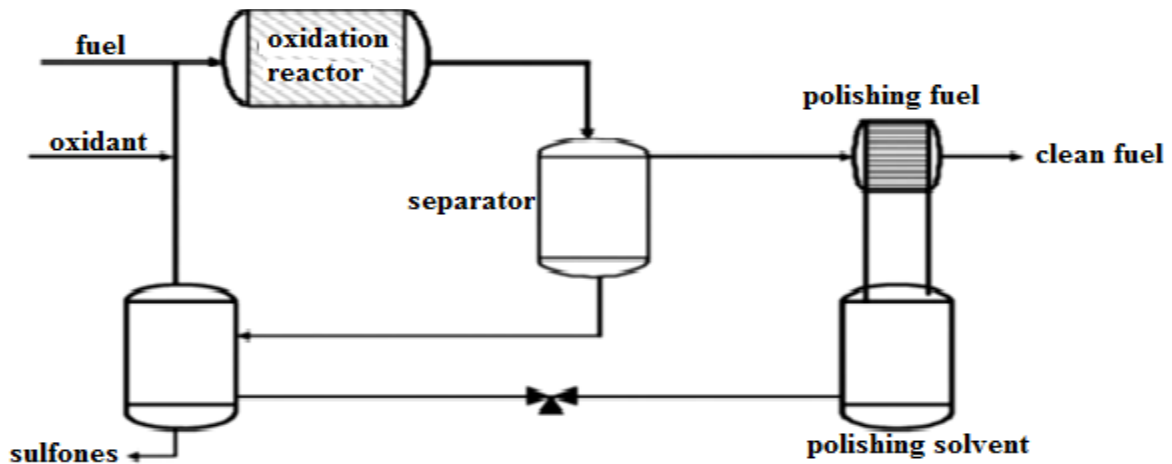


Figure 2.6: Process flow for oil ODS (Campos-Martin et al, 2010)

Campos-Martin et al, 2010 described oxidative desulphurisation as a new and efficient alternative for deep desulphurisation of light oil, as it significantly reduces the sulphur content due to the oxidation of the sulphur. The feasibility of the process for application on both commercial and synthetic diesel oil desulphurisation has been investigated. More than 30 process patents have been issued on the feasibility of the ODS process. Five of the proposed processes have reached commercialization stage; Sulphco process, Lyondell chemicals process; Enichem/UOP process, Unipure process, and PetroStar Process (Stanislaus et al., 2010). Studies proved the feasibility of the oxidation processes to reduce the sulphur content in light oil to 0.1 ppm by weight.

ODS process offers the advantage that the reaction occurs at low temperature and pressure, and that expensive hydrogen is not required in the process. Another advantage of the process is that the refractory S-containing compounds in ODS are easily converted by oxidation. The ODS process ensures maximum sulphur removal with minimal impact on fuel quality (Babich & Moulijn, 2003; Grossman et al. 1999). ODS therefore has great potential as a complementary process to traditional HDS for producing deeply desulphurised light oil (Pawelec et al., 2012). ODS, however, has major drawbacks such as poor selectivity, low yield and loss of heating value of the treated oil (Khalfalla, 2009). To enhance the ODS process and make it more competitive with deep HDS there is need to improve catalytic-specific activity at low $\text{H}_2\text{O}_2/\text{S}$ ratios; increase the mass transfer in a biphasic system containing the oil fraction and polar phase; and enhance the post-treatment of the sulphones produced.

Several ODS systems have been investigated in the desulphurisation of organosulphur compounds and these include: H_2O_2 (oxidant)/polyoxometalate (catalyst) (Te et al, 2001), H_2O_2 /formic-acid (Farhat et al, 2006), H_2O_2 /12-tungstophosphoric-acid (Yazu et al., 2001); H_2O_2 /iron-complexes (TAML, activators) (Mondal et al., 2006); H_2O_2 / Na_2CO_3 , H_2O_2 /acetic-acid (Zannikos & Lois, 1995), H_2O_2 /solid bases (Palomeque et al., 2002), H_2O_2 / (activated-carbon plus formic acid), H_2O_2 /AcOH, H_2O_2 / H_2SO_4 , KMnO_4 and BuOOH (Nanoti et al., 2009) used hydrogen peroxide-formic acid in the desulphurisation of diesel fuel with a sulphur content of 500 ppm and reported that after the oxidization of the sulphur, a complete conversion DBT-sulphones that can be removed easily by either extraction or adsorption can be attained.

Mei et al., (2003) studied the oxidation of dibenzothiophene and diesel fuel with polyoxoperoxo in the presence of H_2O_2 with the assistance of ultrasound irradiation (ultrasound assisted oxidative desulphurisation (UAOD)) and sulphur removal levels of ≈ 98.7 was obtained for diesel fuel. The process consists of four basic steps: the peroxidization and disaggregation of the metal precursor to form anionic peroxometal complex as $\text{W}(\text{O}_2)_n$ in the presence of excess H_2O_2 , phosphotungstic acid; transfer of the peroxometal anion into organic phase by quaternary ammonium salts such as $\text{OC}_4\text{N}^+\text{Br}^-$ with large lipophilic cation. Oxidation of OSCs such as DBT by the peroxometal complex with high efficiency and high selectivity; and reduction of the oxo-species, which dissociate with PTA, and return to the aqueous phase and restores the catalytic cycle (Mei et al., 2003). Ma et al, (2007) investigated the desulphurisation of jet fuel using a combination of the oxidation of the sulphur compounds in the presence of molecular oxygen and a catalytic component, Fe (III) salts, at ambient conditions and the adsorptive desulphurisation of the oxidation-treated fuel over the activated carbon. The catalytic oxidation of the sulphur compounds increased the adsorption of sulphur compounds significantly as ACs showed higher adsorption affinity for both sulphones and sulfoxides compared to thiophenic compounds (Ma et al., 2007). The oxidation reactivity of the sulphur compounds over the Fe (III) salts was found to increase in the order of $\text{DBT} < \text{BT} < 5\text{-MBT} < 2\text{-MBT}$.

Successful implementation of ODS can be achieved in refinery applications by integrating the ODS unit with the existing diesel hydro-treating unit in a revamp situation (Gatan et al., 2004). The UOP/Eni Oxidative Desulphurisation Technology was proposed to be used as a subsequent process to HDS, with the process being carried out in a fixed bed reactor, utilising

organic peroxide as the oxidant and heterogeneous catalysts. An excess of 98% sulphur conversion was reported (Gatan et al., 2004). Sulphone separation is easily done by either extraction or adsorption; the adsorption route was proven to be more cost-effective. However, the high costs of the organic peroxides and their associated handling and storage safety conditions have led to the generation of the peroxides in situ.

2.1.2.6 Biodesulphurisation

Biodesulphurisation (BDS) is another interesting option for the desulphurisation of fuels. As microorganisms require sulphur for their growth and biological activities they are capable of consuming sulphur in thiophenic compounds such as DBT and convert them into sulphones or sulfoxides and thus reduce the sulphur content in fuels. Microorganisms are used for the oxidation of the sulphur compounds and the reaction occurs in the presence of oxygen and water at ambient conditions. BDS removes organo-sulphur compounds present in the fuels while maintaining the carbon structure of the fuel as the microorganism selectively attacks the sulphur atom without assimilation of the carbon content (Darwish, 2015). The process occurs at low temperatures and pressure and has lower capital and operation costs (Javadli & Klerk, 2012) and BDS has been proven to require approximately two times less capital and 15% less operating cost to the conventional HDS process (Kaufman et al., 1998; Javadli & Klerk, 2012). Another advantage of HDS is that in biological activities, biocatalysts (enzymes) are involved making the process more selective.

Klein, et al., (1994) described three primary pathways for DBT desulphurisation; the ring destructive pathway (Kodama pathway), completely destructive pathway and the non-destructive pathway (4S pathway). Both the ring destructive pathway and the complete destructive pathway are not efficient for desulphurisation as they attack the DBT ring and are directed towards the carbon atoms and hence have poor sulphur selectivity (Kodama et al., 1973). To date only two articles have been reported on the ring destructive pathway (Mohebbali & Ball, 2008). In the non-destructive pathway, the carbon ring is not destroyed and the initial catalysis is focused on the sulphur atom for the selective removal of sulphur (Mcfarland, 1999; Marcelis, 2012). Most research has thus focused on the 4S pathway, which can remove sulphur from DBT and its substituted components, specifically 4,6-DMDBT. In the 4S pathway, DBT is oxidised to DBT sulfoxide and then to DBT sulphone,

hydroxyphenylbenzene sulphonate (HPBS) and finally to 2-hydroxylebiphenyl (HBP) (Chen et al., 1998; Folsom et al., 1999; Monticello, 2000; Gupta et al., 2005). While bacteria converting dibenzothiophene and alkyl sulphides are relatively well known, fewer bacteria for benzothiophene were found, and only a few bacteria for thiophene (Pawelec et al., 2012). It has been illustrated that both aerobic and anaerobic microorganisms are effective in desulphurisation while protecting the aliphatic and aromatic contents of the fuel (Mohebbi & Ball, 2008).

Several microorganisms have been investigated for the BDS of petroleum oils and these include *Rhodococcus erythropolis* D-1 and IGTS8, *Rhodococcus* ECRD-1 ATCC 55301, B1, SY1, UM3 and UM9, *Agrobacterium* MC501, *Mycobacterium* G3, *Gordona* GYKS1, *Xanthomonas*, *Nocardia globelula*, *thermophilic Paenibacillus*, *Pantoea agglomerans*, *thermophilic Klebsiella* and some *Cytochrome* P450 species (Agarwal & Sharma, 2010; Monticello, 2000; Javadli & Klerk, 2012) with reported desulphurisation rates of 30–70% from middle distillates, 40–90% from diesel fuels, 65–70% from hydrotreated diesel, 20–60% from light gas oil, 75–90% from cracked stocks, and 20–60% from crude oil (Javadli & Klerk, 2012; Kaufman et al., 1998). Most of the work reported focused on *Rhodococcus* strains and other relatively closely related species, as *Rhodococcus* is particularly well suited for hydrocarbon metabolism (Monticello, 2000). Folsom et al., (1999) investigated the desulphurisation of alkylated dibenzothiophenes using *Rhodococcus erythropolis* and reported extensive desulphurisation of the hydrodesulphurised middle-distillate petroleum with 67 % sulphur reduction in total sulphur from 1850 to 615 ppm and more importantly the sulphur content of 615 ppm cannot be further reduced.

Agarwal & Sharma, 2010 studied the BDS of heavy crude oil and light crude oil using *Pantoea agglomerans* D23W3 (under aerobic and anaerobic condition) and thermophilic *Klebsiella* sp. 13T bacteria. *Klebsiella* sp. 13T was found to show more desulphurisation of LCO than that of HCO and *Pantoea agglomerans* D23W3 was found to be better in BDS. Under anaerobic conditions *P. agglomerans* D23W3 was reported to have a 2% improvement in sulphur removal. On combining ODS with BDS, 91% sulphur removal was reported on heavy oil (Agarwal & Sharma, 2010). Li et al., (2003) investigated the desulphurisation pathway of a facultative thermophilic bacterium *Mycobacterium* sp. X7B on dibenzothiophene (DBT). Total sulphur reduction of 86% was reported on the diesel oil after treatment by resting cells of *Mycobacterium* sp. X7B at 45°C, due to higher mass

transfer. (Grossman et al., 1999) reported 30% sulphur removal from diesel oil by *Rhodococcus* sp. strain ECRD-1 when decane was provided as a carbon substrate to minimize the degradation of hydrocarbons in the diesel oil.

BDS is a green process, and hence is an attractive option compared to the conventional HDS process. The process is however characterized by low bio-catalytic activity and low stability of the bio-catalysts (Nair, 2010; Soleimani et al., 2007). The main challenge in the use of BDS for the production ultra-low sulphur content is the isolation or design of a microbial strain that is characterized by a higher efficiency. Key improvements on the BDS process lie in the enhancement of biocatalyst stability, faster kinetics, minimization of mass transfer limitations and temperature and solvent tolerance approach to attain low sulphur fuels (Pawelec et al., 2012), for the commercial application of the process. Due to limitations on the need to enhance the thermal stability of desulphurisation, the limited transport of the sulphur compounds from the oil to the membrane, the bacterial cell and the limited ability to recover the biocatalyst BDS rates are still low when compared to the HDS and hence implementation of the process on a large scale is still far.

Several researchers (Monticello, 2000); Li et al., 2003; Soleimani et al., 2007) have proposed that BDS can be used in conjunction with the HDS process, either as a pre-process or post-process, in order to achieve ultra-low sulphur levels. Monticello, (2000) suggested a multistage biodesulphurisation, see Figure 2.7. To improve the efficiency of BDS process more research needs to be conducted on increasing the specific desulphurisation activity, hydrocarbon phase tolerance, sulphur removal at higher temperatures, and isolation of new strains for desulphurising a broader range of sulphur compounds (Soleimani et al., 2007). For the viability of the process for deep desulphurisation application there is need for more research to be conducted on:

- (i) production of active resting cells (biocatalysts) with a high specific activity;
- (ii) preparation of a biphasic system containing oil fraction, aqueous phase and biocatalyst;
- (iii) biodesulphurisation of a wide range of organic sulphur compounds at a suitable rate;
- (iv) separation of desulphurized oil fraction, recovery of the biocatalyst and its return to the bioreactor; and
- (v) efficient wastewater treatment (Mohebbi & Ball, 2008).

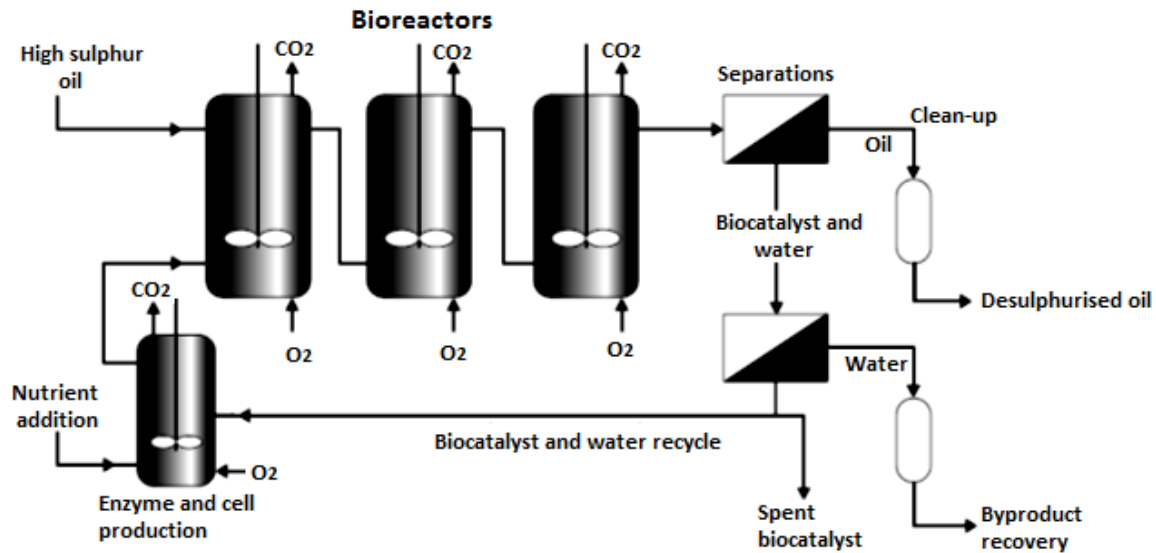


Figure 2.7: A conceptual process flow diagram for the BDS process (Monticello, 2000)

2.1.2.7 Adsorptive Desulphurisation

Adsorptive desulphurisation (ADS) has been identified as one of the most economically attractive techniques for the deep desulphurisation of diesel fuel. Adsorptive desulphurisation is based on a solid adsorbent's capability to selectively adsorb organic sulphur compounds from liquid transportation fuels. The effectiveness of this process relies on the properties of the adsorbent which are; preference to organosulphur compounds over hydrocarbons, retention capacity, endurance, and reactivation (Javadli & Klerk, 2012). Depending on the interaction of the sulphur compounds and the sorbent, ADS can either be 'adsorptive desulphurisation' or 'reactive adsorption desulphurisation (selective adsorption)'. Adsorptive desulphurisation depends on the physical adsorption of organosulphur compounds onto the surface of the adsorbent with reactivation of the sorbent normally done by rinsing the spent sorbent with fresh adsorbent, resulting in a high organosulphur accumulation flow. Reactive adsorption desulphurisation (selective adsorption) makes use of the chemical interaction of the organosulphur compounds and the sorbent where sulphur is adsorbed on the sorbent, as sulphide, and the desulphurised hydrocarbon is emitted into the desulphurised fuel stream. Compared to physical adsorption chemisorption is highly specific and the adsorption energies are generally substantially greater than those for physical adsorption (Karge & Weitkamp, 2008). Table 3 shows a comparison of physical adsorption to chemical adsorption.

Table 3: Physical adsorption and chemisorption (Karge H.G, & Weitkamp J., 2008)

Physical adsorption	Chemisorption
Low heat of adsorption (1.0 to 1.5 times latent heat of evaporation)	High heat of adsorption (> 1.5 times latent heat of evaporation)
Nonspecific	Highly specific
Monolayer or multilayer	Monolayer only
No dissociation of adsorbed species	May involve dissociation
Only significant at relatively low range temperatures of temperatures	Possible over a wide range temperatures of temperatures
Rapid, nonactivated, reversible	Activated, may be slow and irreversible
No electron transfer, although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface

Physical adsorption is based on Van der Waals forces and electrostatic forces in molecules with a permanent dipole moment. Van der Waals forces that attract the molecule to the surface do not change the adsorbate molecule and are usually weak. With chemical adsorption (chemisorption), chemical bonds are formed between the adsorbate molecule and the surface as a result of one or more free valences on the surface of an adsorbent material resulted from the broken covalent bonds between atoms at the surface. Chemisorption involves molecular interactions with free valences, which leads to a monolayer coverage on the surface of the adsorbent. According to Do, (1988), adsorption separation is based on three main mechanisms: steric, equilibrium and kinetic. Steric mechanism involves the adsorption of small molecules over large molecules, equilibrium mechanism involves the solid medium's ability to accommodate different species according to the strength of the adsorbing species and kinetic separation mechanism is based on the rate of diffusion of different species

into the pores. As ADS can be carried out at normal operating conditions, it is generally inexpensive.

The adsorption process of sulphur compounds is affected by the size, shape and molecular weight of solute, the electrostatic charge on the surface of solute molecule and the site of the solid matrix where adsorption takes place, shape of the binding site of the solid matrix and the polarity of the solute molecule and the binding site of the solid matrix. The pore size of the microspores is also critical as it determines the accessibility of adsorbate molecules to the internal adsorption surface especially for zeolites and carbon molecular sieves (Alavi & Hashemi, 2014). The adsorbent's properties such as the adsorption capacity, surface area and selectivity are directly affected by their structure and composition and may be enhanced by modifying their preparation methods and conditions.

2.1.2.7.1 Adsorbents

Various adsorbents have been evaluated in the desulphurisation and these include activated carbon, activated alumina, metal sulphides, zeolites (Ng et al., 2005), silica gel, zeolite molecular sieves, carbon molecular sieves, impregnated carbons (Cu-chlorides - CO separation), clays (natural and pillared clays), resins, polymers (biological, ions, large molecules), polymer supported adsorbents (Fadhel, 2010b) π -complexation sorbents (Cu(I)-Y, Ag-Y, CuCl/g-Al₂O₃, AgNO₃/SiO₂) (Hernandez-Maldonado & Yang, 2004), metal-organic framework adsorbents (Blanco-Brieva et al., 2010), CeO₂-based adsorbents (Watanabe et al., 2004) carbon nanotubes (Alavi & Hashemi, 2014) as well as nickel based adsorbents (Ma et al., 2005; Kim et al., 2006).

Activated carbon has been intensively applied in the desulphurisation of different fuels. Research has focused on the adsorption of BT, DBT, and 4,6-DMDBT using different types of activated carbons, including oxidized and metal-impregnated adsorbents (Zhang et al., 2012; Ania & Bandosz, 2006; Seredych & Bandosz, 2011). Application of low temperature oxygen plasma (Zhang et al., 2012), increasing the adsorbent's pore sizes (Seredych et al., 2009a), the presence of acidic groups and supports on the activated carbons (Selvavathi et al., 2009) significantly improves the activated carbons' adsorption capacity.

To improve their adsorption efficiencies various adsorbents have been modified and applied in desulphurisation; ion/metal impregnated adsorbents (activated carbons, zeolites,

mesoporous materials) (Ahmad et al., 2014; Moosavi et al., 2012; Xiao et al., 2010; Xiao et al., 2008; Seredych & Bandosz, 2010; Meng et al., 2010; Hernandez- Maldonado & Yang, 2004a); oxidised and nickel supported adsorbents (Zhou et al., 2009; Selvavathi et al., 2009); metal on metal based adsorbents (Ma et al., 2005); reactive adsorbents (formaldehyde, phosphotungstic acid and mesoporous silica gel) (Wang et al., 2012); π -complexation adsorbent on zeolite (Hernandez-Maldonado & Yang, 2003) combination of ZSM-5/13X zeolites (Hu et al., 2003); metal-loaded polystyrene-based activated carbons (Ania & Bandosz, 2006). Transition metals (Cu, Ni, Ag, Zn, Fe, and Pd) or in some case noble metals (Pt and Pd) have been impregnated on different adsorbents (zeolites, alumina, silica and activated carbon) to enhance the adsorption properties of the adsorbents for better adsorption capacities for thiophenic compounds from commercial and model fuels (Xiao et al., 2010; Meng et al., 2010; Ania & Bandosz, 2006; Seredych & Bandosz, 2009b; Seredych & Bandosz, 2011).

The bulk of the research on adsorbers for fuel desulphurisation has focused on activated carbon and alumina and several other adsorbents. Very few articles have been reported on the desulphurisation of diesel fuel using N-halogen compounds (alkali metal salts of sulphonamides) i.e. chloramine T (sodium N-chloro-p-toluene sulphonamide) and PI agent (sodium N-chloro-polystyrene sulphonamide) (Fadhel, 2010b; Shiraishi et al., 2002). N-halogen compounds have been found capable of removing sulphur compounds through liquid-liquid adsorption processes or reactive adsorption (Ou, 1992) and are hence of much interest. Reported N-halogen compounds in the desulphurisation of fuels were by (Ou, 1992; Shiraishi et al., 2001; Shiraishi et al., 2002) using Chloramine T; and (Fadhel, 2010a; Matoro, 2016) using PI.

Shiraishi et al., (2001) studied the desulphurisation of model light oil and its methyl-substituted DBTs using chloramine T and reported the desulphurisation reactivity to be of the order 4,6-dimethyl > 4-methyl > DBT. They concluded that the rate of the chlorination depends on the electron density (nucleophilicity) on the sulphur atom for DBTs, and as a result, methyl-substituted DBTs, having high electron density are desulphurised more easily than the non-substituted DBT. On application of the process to actual light oil (0.19 wt% sulphur content), ultra-low sulphur levels (0.05 wt%) could not be attained due to the accumulation of the produced sulphimides during the reaction (Shiraishi et al., 2001; Shiraishi et al., 2002).

Shiraishi & Naito et al., (2003) studied the desulphurisation of light oil using a polymer-supported imidation agent (PI, sodium N-chloro-polystyrene sulphonamide) and reported adsorption of sulphur compounds by the PI, and successful removal of the sulphur compounds from the oil. The polymer obtained was insoluble to the solution and hence could be recovered by filtration. They also reported that the sulphur concentration of commercial light oil was decreased successfully from 400 ppm to less than 50 ppm (ultra-deep desulphurisation level). Desulphurisation using the PI agent unlike with Chloramine T, does not require subsequent removal of produced sulphimides, and the sulphur level was successfully reduced to less than 50 ppm (ultra-deep desulphurisation) (Gawande & Kaware, 2014; Fadhel, 2010b). It was reported that deep desulphurisation levels could be successfully achieved for diesel oil using polymer supported imidation agent (PI) at ambient conditions and at sorbent dose beyond 0.25 (mg/) for sulphur concentrations less than 12354ppm (Fadhel, 2010b).

The reaction of the sulphur compounds with the alkali metal salts of sulphonamides results in the formation of sulphimides which requires subsequent adsorption (Trost & Melvin, 1975; Gilchrist & Moody, 1977; Mann & Pope, 1922) from solution. The sulphimides have been reported to have antimicrobial, diuretic and hypotensive properties on tumor growth and activity as antidepressants and stimulants of the central nervous system (Trost & Melvin, 1975). Of interest is the use of the recovered sulphimides from the desulphurisation process, as novel materials for medicinal supplies (Shiraishi et al., 2001). To add on to the knowledge based on the use of adsorption as a desulphurisation technology this research will focus on the use of a polymer supported imidation agent as the adsorbent for the selective removal and adsorption of sulphur compounds from diesel fuel.

2.1.2.7.2 Adsorption column studies

Several papers (Kim et al., 2006; Mužic et al, 2009b; Mužic et al., 2010b; Mužic et al, 2011; Bhattacharyulu et al., 2012) have reported the study of fuel desulphurisation in adsorption columns and these includes both batch column studies and continuous fixed bed column studies. Ng et al, (2005) studied the desulphurisation of model sulphur compounds in a hexadecane solution using commercial zeolites, NaY, USY, HY and 13X, by adsorption and flow calorimetry techniques. NaY was found to have the highest sorption capacity. Velu et al., (2002) investigated the selective desulphurisation of jet fuel over transition metal ions

(Ni, Cu, Zn, Ce, Pd, H) exchanged NH_4 Y-zeolites in a batch reactor and reported Ce exchanged and Pd-exchanged zeolites to exhibit better sulphur adsorption capacity (50 to 60 %). Hernandez-Maldonado & Yang, (2004) studied the removal of thiophene in commercial diesel fuel, from the simulated feedstock using Cu(I)-Y and Ag-Y zeolites in a fixed-bed adsorber operated at ambient temperature and pressure; nickel(II)-zeolites showed higher sulphur selectivity and capacity due to π -complexation.

Bhattacharyulu et al., (2012) carried out unsteady state adsorption column studies for the desulphurisation of hydrocarbon liquid fuel on activated carbon in a fixed-bed adsorber with continuous flow of feed. They went on to investigate the effect of the feed flow rate, feed solution concentration, and adsorbent bed height on rate of adsorption and reported the increase in feed flow rate to decrease adsorption zone height, at all concentration studied. They also concluded that when increasing amounts of fluid are passed through such a bed, the solid adsorbs increasing amounts of solute, and an unsteady state prevails. Bu et al., 2011 carried out adsorption experiments in batch and fixed bed adsorption systems for real and model diesel fuels containing sulphur and aromatic compounds and concluded that for effective adsorption of large molecules pore size of adsorbent should be sufficiently large to reduce diffusional resistance.

Kim et al., (2006) carried out experiments on the denitrogenation and desulphurisation of diesel fuel using supported Ni activated alumina and activated carbon, in a fixed bed adsorption system, and reported activated carbon to have more selectivity and capacity for the adsorption of the sulphur (especially for the sulphur compounds with methyl substituent's, such as 4, 6- methyl dibenzothiophene and nitrogen compounds. The kinetic and equilibrium analysis of the desulphurisation of diesel fuel using activated carbon and Al_2O_3 was investigated by Mužic et al., (2009b). They reported the experimental and calculated data to coincide better with the Ho model rather than the Lagergren model and the Freundlich isotherm model to better fit the data over the Langmuir model (Mužic et al., 2009b). They went on to carry out the statistical analysis of the data obtained using the 2^3 factorial design, to determine the influence of time, initial, sulphur concentration, activated carbon mass and their interactional effects on sulphur content and adsorption capacity.

Yang et al., (2003) studied the desulphurisation of transportation fuels on two adsorption beds to enhance the adsorption capacity and reported the best combination of layered beds to be activated carbon/activated alumina/ Cu(I)-Y (Hernandez- Maldonado & Yang, 2004b).

Mužic et al., (2010c) studied the kinetic characterization of diesel desulphurisation adsorption process by applying the Lagergren's pseudo-first order, pseudo-second order and intraparticle diffusion models and reported the best fit to be with the pseudo second order model and the data fit the Freundlich isotherm. Statistical analysis of the process was also carried out according to three-factor two-level factorial design. Mužic et al., (2010a) carried out an investigation on the adsorptive desulphurisation of diesel fuel in a batch adsorption apparatus, using Chemviron Carbon SOLCARBTM C3 activated carbon as the adsorbent applying two DOE (design of experiment) methods, full factorial designs and Box-Behnken designs. They also studied the effects of individual factors and their interactions on the sulphur concentration and sorption capacity, and developed statistical models of the process. Second-order models were found to give reasonably good description of the system and they reported the lowest achieved output sulphur concentration as 7.6 mg kg^{-1} with relatively low sorption capacity of 0.0861 mg/g (Mužic et al., 2010b).

Mužic et al., (2010b) modelled the adsorptive diesel fuel desulphurisation on activated carbon, assuming the mass transfer rate as the rate limiting step. Adsorptive desulphurisation experiments were carried out in the fixed-bed adsorption column to validate the fixed-bed adsorption model's adequacy in predicting the breakthrough curves. They reported the best experimental results giving the lowest output sulphur concentration of below 0.7 mg kg^{-1} and the longest breakthrough time of 11.8 h, were achieved for a feed flow of $1.0 \text{ cm}^3 \text{ min}^{-1}$, a bed depth of 28.4 cm and a temperature of $50 \text{ }^\circ\text{C}$. Mužic et al., (2011) went on to investigate the potential of commercial application of the fixed bed adsorptive desulphurisation, by simulation of an industrial adsorption column, and reported the typical column dimensions and adsorbent load and these values were in good agreement with the ones reported in literature (Mužic et al, 2009b; Mužic et al, 2011).

Regeneration of the spent adsorbent is an important factor in adsorption processes and can be carried out either in-situ or ex-situ to the adsorption vessel to an extent that the adsorbents can be reused. Solvent regeneration in adsorption processes can be done by temperature or pressure swing. Reactivation of the spent sorbent results in sulphur elimination as H_2S , S, or sulphur oxides, depending on the process applied (Babich & Moulijn, 2003). The overall efficiency of the desulphurisation process is mainly determined by the adsorbent properties: its adsorption capacity, selectivity for the organic-sulphur compounds, durability and regenerability (Salem & Hamid, 1997).

The intended study will focus on the adsorptive desulphurisation of diesel fuel using a polymer supported imidation agent and add on to the knowledge base within this field. There has not been sufficient work addressing the simulation and modeling of adsorptive desulphurisation of transportation fuels, in particular using the polymer supported agent as the adsorbent. This work is going to focus on developing a model for the simulation of the adsorptive desulphurisation of diesel fuel.

2.1.2.7.3 Developments in adsorption

Recent advances in the adsorptive desulphurisation of transport fuels have been reported. Phillips Petroleum proposed the S-Zorb diesel desulphurisation process which is an extension of their S-Zorb process for gasoline (Song & Ma, 2003). The process makes use of a solid sorbent in a fluidised bed reactor at relatively low pressures and temperature in the presence of hydrogen and modified zinc oxide to produce ULSD. Sulphur from the sulphur compounds is carried over to hydrogen sulphide, which was by chemisorption bound with zinc oxide as zinc sulphide. The S-Zorb process is however not feasible for treating untreated distillate streams, as it can treat distillates containing 500 ppm weight sulphur or less. At Penn State University, a process called PSU-SARS (Penn State University- Selective Adsorption for Removal of Sulphur), has been developed which utilises various types of adsorbents to selectively remove sulphur molecules from liquid transportation fuels (Song, 2003; Song & Ma, 2003). The process allows for the removal of only the sulphur, which comprises less than 1 percent of the fuel, while leaving the more prevalent aromatics behind, with the key being the design of adsorbents possessing surface sites that selectively interact with sulphur in the presence of aromatics (Velu et al., 2003) at ambient temperature without using hydrogen or any other reactive gas.

Related articles on the desulphurisation of diesel fuel using PI have focused on the feasibility of the PI for the desulphurisation of diesel fuel, the effect of feedstock quality and sorbent dose on adsorption capacity (Fadhel, 2010b) and investigation of the effect of the adsorption process parameters on the sulphur removal efficiency of the synthesized PI (Matoro, 2016). This work is going to focus on the simulation of the adsorptive desulphurisation process of diesel fuel using PI (reactive adsorption process that involves the chemical interaction between the adsorbent and the sulphur compounds), using MATLAB. The simulation model will allow for further investigation of the feasibility of using the PI agent for the

desulphurisation of diesel fuel, as well as provide the optimum conditions for industrial application of the adsorption process.

2.2 Adsorption Equilibria

Adsorption is the accumulation of molecules onto an interfacial layer and is often described using isotherms. An adsorption isotherm gives the equilibrium relationship between the amount of adsorbate retained and the amount of adsorbate in solution at a constant temperature. It describes the mechanism controlling the retention or adsorption of an adsorbate from an aqueous porous media onto a solid phase (Foo & Hameed, 2010). Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb on to a surface is equal to the rate at which they desorb. As the physical chemistry involved in adsorption is rather complex, no single theory can be used to sufficiently fit all systems. Of value is an accurate representation of the equilibrium of the adsorption process and the treatment of each system separately. Adsorption equilibria for liquid/solid systems is not well understood as is the case with gas/solid systems (Richardson et al., 2002) and more research needs to be directed at adsorption of liquid/solid systems.

Based on the interaction of three properties namely the concentration of the sulphur in the liquid phase, the concentration of the sulphur in the solid phase and the temperature of the system; the adsorption equilibria can be determined by keeping one of the three properties constant, normally the temperature. A plot of the concentration of the adsorbed sulphur at equilibrium, C_e versus the adsorption capacity in equilibrium q_e gives the adsorption isotherm. The equilibrium behaviour of an adsorption process guides the development of a mathematical model for the process (Weber & Smith, 1987). Adsorption equilibrium data provides the basis for assessing the adsorption processes and, in particular, for adsorber design (Worch, 2012). Data on the equilibrium in a considered adsorbate/adsorbent system is critical for the characterization of the adsorbability of the sulphur pollutant in the diesel fuel, the selection of an appropriate adsorbent, and the appropriate adsorber design.

Breakthrough isotherms derived from predictive dynamic models are particularly sensitive to equilibrium parameters (Weber & Smith, 1987) both in the low and very high equilibrium concentrations (Crittenden et al., 1987; Mc Kay & Al Duri, 1989). Hence in the formulation of models, it is crucial to select an equilibrium model that accurately describes single-solute

isotherm data over wider ranges of concentration and that can be translated into a predictive multicomponent isotherm equation; and the model selected must be integrable with dynamic models for more accurate results.

2.2.1 Adsorption Isotherms for single component equilibria

Adsorption isotherms give the equilibrium relationship established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. Single-component adsorption involves the adsorption of one adsorbate component from a system. At very low concentrations the molecules adsorbed are widely spaced over the adsorbent surface and molecules have no influence on one another. For these limiting conditions it is reasonable to assume that the concentration of the adsorbed phase, C_s is proportional to the concentration of the adsorbate in the fluid, C ; given by :

$$C_s = K_a C \quad (2.2)$$

The proportionality constant, K_a obeys the van't Hoff equation and is given by:

$$K_a = K_o e^{-\frac{\Delta H}{RT}} \quad (2.3)$$

Where:

K_o is the equilibrium constant at absolute temperature;

ΔH is the standard enthalpy change;

R is the gas constant; and

T is temperature.

The equilibrium adsorption isotherms describe the relationships between the equilibrium concentration of the adsorbate in the solid and liquid phase at constant temperature. Single component adsorption isotherms can be generally characterized by some typical curves/shapes; linear, favorable, strongly favorable, irreversible and unfavorable which are shown in Figure 2.8.

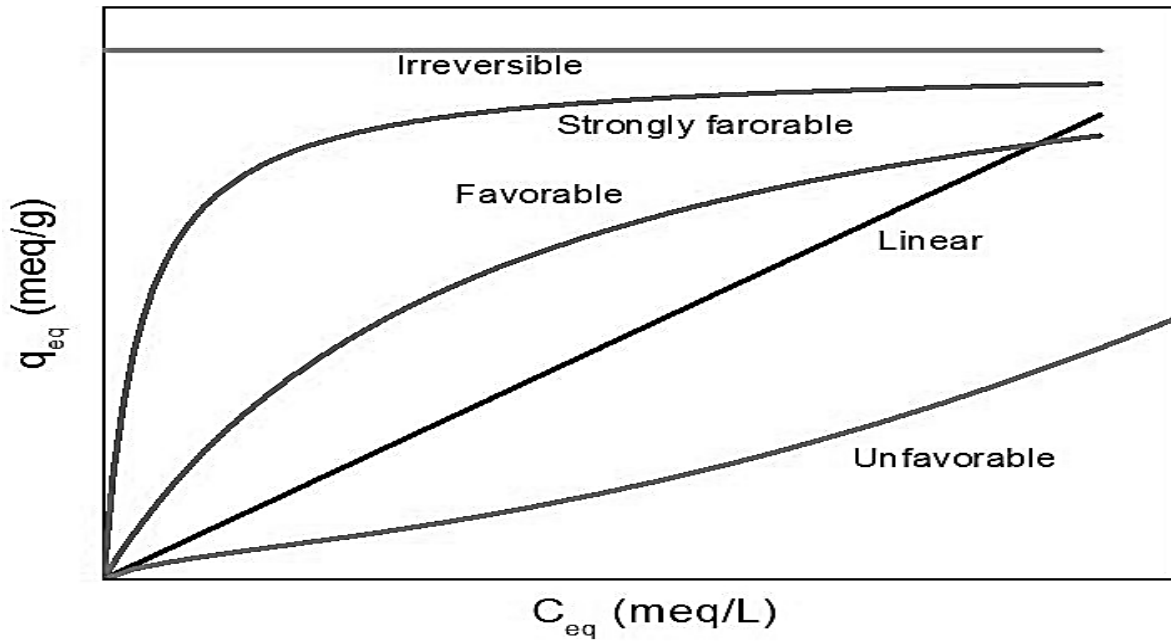


Figure 2.8: Adsorption isotherms (Barros et al., 2013)

2.2.1.1 Linear Adsorption Isotherm

The linear adsorption isotherm is the simplest and most widely used type of adsorption isotherm. It is expressed as:

$$q_e = K_d C_e \quad (2.4)$$

Where:

q_e is the concentration of solute adsorbed onto the solid phase;

K_d is the distribution coefficient and

C_e is the concentration of the solute in solution

It generally assumes that the distribution coefficient is constant and forms the basis of the general retardation factor. The distribution coefficient applies well when applied to trace concentrations of unionized hydrophobic organic molecules but is not suitable in organic contaminants due to its sensitivity to aqueous chemical conditions (Goldberg et al., 2007; Kohler et al., 1996).

2.2.1.2 Freundlich Adsorption Equation

The Freundlich isotherm does not have much limitation as it can fit both homogeneous and heterogeneous surfaces, and both physical and chemical adsorption. This model has frequently been applied in depicting the adsorption behaviour of organic compounds and reactive matters (Xu et al., 2013). The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems and is expressed as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2.5)$$

Where:

q_e is the concentration of solute adsorbed onto the solid phase,

K_F is an indicator of adsorption capacity,

C_e is the concentration of the solute in solution

To determine the constants K_F and n , the linear form of the equation may be used to produce a graph of $\ln(q_e)$ against $\ln(C_e)$.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2.6)$$

The Freundlich isotherm was found to perfectly fit adsorption data for the adsorption of dyes (El-Latif et al., 2010; Mc Kay & Al Duri, 1987; Namasivayam & Yamuna, 1995), metals (Bhattacharya & Venkobachar, 1984; Che-Galicia et al., 2014), oxygenated pollutants (Annesini et al., 2000) and organic pollutants (Fernandez et al., 1996). The Freundlich isotherm model has perfectly fit experimental data for the desulphurisation of sulphur compounds from fuels on application of different adsorbents (Mužic et al., 2010c; Mužic et al., 2009b; Adekanmi & Folorunsho, 2012).

2.2.1.3 Langmuir adsorption model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer (chemical adsorption) of solute molecules on the

adsorbent surface, with no lateral interaction between the adsorbed molecules (Vijayaraghavan et al., 2006; Foo & Hameed, 2010). It refers to homogeneous adsorption and assumes all sites possess equal affinity for the adsorbate and the adsorption heat does not vary with the coverage (Kundu & Gupta, 2006; Xu et al., 2013). Adsorption is assumed to take place when a free adsorbate molecule collides with an unoccupied adsorption site and each adsorbed molecule has the same percentage to desorption (Langmuir, 1916). The Langmuir isotherm has been found to fit well with most liquid/solid adsorption processes (Sigrist et al., 2011; Otero et al., 2005; Tan et al., 2008) and specifically diesel desulphurisation processes (Mužic et al., 2010b). Due to its simplicity and ability to well-fit most performances, the Langmuir isotherm has become one of the most popular models in adsorption studies (Xu et al., 2013).

The Langmuir model expression is given:

$$q_e = \frac{Q_m K C_e}{1 + K C_e} \quad (2.7)$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbate per unit mass of sorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively. Q_m is the maximum amount of the adsorbate per unit mass of sorbent to form a complete monolayer on the surface bound at high C , and K is a constant related to the affinity of the binding sites (L/mg).

The Langmuir equation can be described by the linearized form:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad (2.8)$$

Plotting the specific adsorption $\frac{C_e}{Q_m}$ against the equilibrium concentration C_e gives the adsorption capacity and the Langmuir constant. The Langmuir equation relatively describes physical or chemical adsorption well on solid surfaces with one type of adsorption active site. Many authors have reported the Langmuir isotherm model to fit the adsorption of organic sulphur compounds (Jiang et al., 2003; Zhang et al., 2012; Zhou et al., 2006; Bhattacharyulu et al., 2012; Xiao et al., 2008; Xiong et al., 2012).

2.2.1.4 Temkin Adsorption model

Temkin and Pyzhev, (1940) considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with Redlich-Peterson Model. The Temkin isotherm has been generally applied in the following form:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (2.9)$$

and can be linearized as:

$$q_e = B \ln A + B \ln C_e \quad (2.10)$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K).

A plot of q_e versus $\ln C_e$ gives the constants A and B .

2.2.1.5 BET (Brunauer-Emmett-Teller) Equation

This is a more general, multi-layer model isotherm model. It assumes that a Langmuir isotherm applies to each layer and the BET (Brunauer, Emmett and Teller) isotherm applies between the layers (Braunauer et al., 1938) and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer. It is expressed by the equation:

$$q_e = \frac{K_B C_e Q^o}{(C_s - C_e) \{1 + (K_B - 1)(C_e/C_s)\}} \quad (2.11)$$

Where:

C_s is the saturation (solubility limit) concentration of the solute,

K_B is a parameter related to the binding intensity for all layer,

As $C_e \ll C_s$ and $K_B \gg 1$ and $K_{ad} = K_B/C_s$ BET isotherm approaches Langmuir isotherm.

2.2.1.6 Other Adsorption Isotherms

Several isotherms combine aspects of both the Langmuir and Freundlich equations – the Toth isotherm, Radke-Prausnitz isotherm, Sips isotherm e.t.c (Levan et al., 2008). However the unpopularity of these isotherms does not mean they are unuseful. The Dubinin-Radushkevich isotherm is able to calculate the mean adsorption free energy from which the prediction of adsorption type is available (Dubinin & Radushkevich, 1947) and the Temkin isotherm allows one to estimate the effect of temperature (Temkin & Pyzhev, 1940). The single-component isotherms have been summarized in several studies and based on the linear expression of each isotherm, all the isotherm parameters can be acquired by linear regression (Xu et al., 2013).

Modified Langmuir isotherms e.g the Langmuir-Freundlich isotherm have been reported as the suitable isotherm models for the adsorption of sulphur compounds in several articles (Jeppu & Clement, 2012; Ania & Bandosz, 2006; Nair, 2010; Moosavi et al., 2012; Deliyanni et al., 2009; Hernandez-Maldonado & Yang, 2004).

2.2.1.7 Multi-component Isotherms

For the adsorption of a variety of pollutants within a system, single-component isotherms are unable to describe the adsorption equilibrium since competitive adsorption occurs between different species. Whereas the above described isotherms are more suitable for single component adsorption systems, multi-component isotherms were developed for multi-component adsorption systems. These include ideal adsorbed solution theory (IAST), multicomponent Langmuir isotherm (Karge & Weitkamp, 2008; Silva et al., 2010) and multicomponent Langmuir-Freundlich isotherm (Ruthven, 1984). According to (Myers & Prausnitz, 1965; Radke and Prausnitz, 1972), the IAST model is based on the equivalence of the spreading pressure, π , of each component and is one of the most reliable isotherms.

2.2.2 Adsorption Kinetics

In addition to the adsorption capacity the kinetic performance of an adsorbent is of great value in design of adsorption processes. The kinetic analysis provides the rate of solute uptake, which determines the residence time required for completion of adsorption reaction. Based on the kinetic information, the scale of the required adsorption apparatus can be evaluated. Basically, adsorption kinetics is core in determining the efficiency and performance of fixed-bed or any other flow-through systems (Qiu et al., 2009). The kinetics of adsorption may be controlled by several independent phenomena. These can work in series or parallel and they often fall in one of the following general categories: bulk diffusion, external mass transfer (film diffusion), chemical reaction (chemisorption) and intra-particle diffusion (pore diffusion). Several kinetic analyses are being applied to adsorption and not only they express the adsorption rates but also give indications of possible adsorption mechanisms.

Adsorption diffusion models are always built on the basis of three consecutive steps: diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion; diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion; and adsorption and desorption between the adsorbate and active sites, i.e., mass action (Lazaridis & Asouhidou, 2003). Adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above (Qiu et al., 2009).

Adsorption and desorption processes are a critical component in many heterogeneous systems and have been investigated extensively. As adsorption and desorption processes are time-dependent, it is necessary to know the rate of adsorption for the proper design and evaluation of adsorbents. The desorption rate is important in the design and reactivation of the adsorbent. It is thus of importance to recognize and understand the adsorption and desorption kinetics and determine their phenomenological coefficients characterizing the transport of adsorbents within adsorbates (Cheung et al., 2000).

To gain proper understanding there is need for proper understanding of the adsorption equilibria and kinetics. Adsorption thermodynamic data only provides information about final state of a system, but it is the kinetic data that defines the changes in chemical properties with time and rates of changes. Adsorption kinetics studies reported in literature include studies on: theoretical applications of adsorption (Ceyrolles et al., 2002; Panczyk & Rudzinski, 2002; Rudzinski, 2002); adsorption of ions (Ho & Mckay, 1998b; Ho & Mckay, 1999; Ho et al., 1996; Cheung et al., 2000); adsorption of organic compounds (Ho & McKay, 1998c; Ho & Mckay, 1998a; Annesini et al., 2000; Chern & Chien, 2001); and gas adsorptions (Anisuzzaman et al., 2014; Sankararao & Gupta, 2007).

Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics (Ho, 2006). The sorption process can be described by four consecutive steps:

1. transport in the bulk of the solution;
2. diffusion across the liquid film surrounding the sorbent particles;
3. particle diffusion in the liquid contained in the pores and in the sorbate along the pore walls;
4. sorption and desorption within the particle and on the external surface (Ho et al., 2000).

Any of the four previous steps may be the rate controlling factor or any combination of the steps. It is important to note that in large scale adsorption processes, transport in the solution is sometimes the rate determining step.

2.2.2.1 Adsorption Reaction Models

These assume the rate of surface reaction to be the rate-limiting step. Adsorption reaction models have been widely developed and applied to describe the kinetic process of adsorption of dyes (Lazaridis et al., 2003; Tan et al., 2008), pesticides (Hamadi et al., 2004), phenols (Jain et al., 2004; Namasivayam & Kavitha, 2016), heavy metal ions (Chen et al., 2008) and inorganic compounds (Huang et al., 2008). Specifically for the adsorption of organic sulphur compounds various articles have reported use and application of adsorption reaction models (Khodadadi et al., 2012; Mužic et al., 2010c).

2.2.2.1.1 Pseudo First Order Rate Equation

Believed to be the earliest model pertaining to the adsorption rate, the first order rate was proposed by Lagergren, (1898) to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, based on the adsorption capacity.

It can be presented as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.12)$$

Where: q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model. Introducing boundary condition $q_t(t = 0) = 0$ and integrating gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2.13)$$

The driving force for the reaction is expressed as the difference between the final equilibrium loading (which is constant for a given initial concentration and adsorbent dose) and the loading time (Worch, 2012). Reaction kinetic models are reasonable mostly only for weakly porous adsorbents where slow surface reactions (chemisorption) play a major role and film diffusion does not exist. The pseudo first order model has been widely used to describe the adsorption of pollutants from wastewater (Tan et al., 2008; Hameed & El-khaiary, 2008). The pseudo-first order equation is however mostly unable to describe kinetic data as well as the pseudo-second order equation (Plazinska et al., 2009; Kosasih et al., 2010; Hameed et al., 2008) and opposite cases reported are rather scarce (Mohanty et al., 2008).

2.2.2.1.2 Pseudo Second Order Rate Equation

The pseudo-second order kinetics is used to define the kinetic behaviour of an adsorption process with the rate of direct adsorption/desorption process (seen as a kind of chemical reaction) controlling the overall sorption kinetics (Plazinska et al., 2009). The pseudo second

order model was first proposed for describing the kinetics of heavy metal removal by natural zeolites (Blanchard et al., 1984). This was based on the assumption that the rate of the ion exchange reaction occurring on the surface is responsible for the removal kinetics and that the kinetic order of this reaction is two with respect to the number of adsorption sites available for the exchange.

The most commonly-applied form of the pseudo-second order equation is that presented by Ho (Ho et al., 1996). The pseudo second order rate equation was described by Ho for the adsorption of divalent metal ions onto peat (Ho & McKay, 1998c), in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat. The pseudo second order equation is given by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.14)$$

Where: k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the rate constant of the pseudo-second-order model for the adsorption process, q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively.

Integrating and applying boundary conditions ($t = 0$ and $q_t = q_e$ to $t = t$ and $q_t = q_t$), gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2.15)$$

The rate constant k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) and q_e^2 (mg/g) can be obtained from the intercept and slope of the linear plots of $\frac{t}{q_t}$ against $\frac{t}{q_e}$.

This equation has been successfully applied to the adsorption of metal ions (Ho & McKay, 1999; Tan et al., 2008; El-Latif et al., 2010; Suteu & Malutan, 2012), dyes (Tan et al., 2007; Hameed et al., 2008; Suteu & Malutan, 2012), phenols (Jain et al., 2004; Mohanty et al., 2008; Namasivayam & Kavitha, 2016), oils (Mowla et al., 2013), inorganic (Huang et al., 2008) and organic substances from aqueous solutions (Leyva-Ramos et al., 2007).

Ayanda et al., 2012 used the pseudo first-order and pseudo second-order kinetic models in simplifying the calculation of the adsorbate uptake rate and developed the relationship needed for particle diffusion-controlled adsorption. Many experimental studies and the extensive use of the pseudo second order model have revealed that the value of k_2 strongly depends on the applied operating conditions. The influence of experimental factors on k_2 , are discussed on the basis of sorption systems for which such dependencies on initial solute concentration, pH of solution, temperature and agitation rate have been taken into account. Khodadadi et al., (2012); Mužic et al., (2009a) reported the kinetic study for the desulphurisation of diesel fuel as being amply given by the pseudo second order.

2.2.2.1.3 Elovich's equation

The Elovich equation of chemisorption, based on adsorption capacity, was proposed by Zeldowitsch, (1934) for describing the rate of adsorption of carbon monoxide on manganese dioxide that decreases exponentially with an increase in the amount of gas adsorbed (Ho, 2006). The equation is often valid for systems in which the adsorbing surface is heterogeneous (Namasivayam & Kavitha, (2002), and is expressed as:

$$\frac{dq}{dt} = ae^{-\alpha q} \quad (2.16)$$

where q represents the amount of gas adsorbed at time t , a the desorption constant, and α is the initial adsorption rate. Eq.(2.15) can be rearranged to a linear form, giving:

$$q = \frac{2.3}{\alpha} \log(t + t_o) - \frac{2.3}{\alpha} \log t_o \quad (2.17)$$

with:

$$t_o = \frac{1}{\alpha a} \quad (2.18)$$

The Elovich's equation has been widely used to describe the adsorption of gas onto solid systems (Heimberg et al., 2001). The model has been applied to describe the adsorption process of pollutants from aqueous solutions (Cheung et al., 2000).

2.2.2.1.4 Second-order rate equation

The typical second-order rate equation in solution systems is (Qiu et al., 2009):

$$\frac{dC_t}{dt} = -k_2 C_o^2 \quad (2.19)$$

Where; C_o and C_t (mg/L) is the concentration of solute at equilibrium and at time t (min), respectively, and k_2 (L/(mg·min)) is the rate constant.

The second-order rate equation has been reasonably applied to describe adsorption reactions in soil and soil minerals. It has also been used to describe fluoride adsorption onto acid-treated spent bleaching earth (Mahramanlioglu et al., 2002) and phosphamidon adsorption on an antimony(V) phosphate cation exchanger (Varshney et al., 1996).

2.2.2.1.5 Langmuir-Hinshelwood Kinetics

The Langmuir-Hinshelwood mechanism is based on the rate of the heterogeneous reaction being controlled by the reaction of the adsorbed molecules, with all adsorption and desorption pressures being in equilibrium. The Langmuir-Hinshelwood kinetic expression has been applied to describe the sorption kinetics of metal ions onto humic acids. The Langmuir-Hinshelwood equation is expressed as follows:

$$\frac{-dC_t}{dt} = \frac{k_1 C_t}{1 + k_2 C_t} \quad (2.20)$$

Where: C_t is the surface concentration of occupied sites, m^{-2} ; k_1 and k_2 are the initial and final kinetic constants for the surface reaction, s^{-1} .

Rearranging the equation gives:

$$\frac{\ln \frac{C_o}{C_t}}{C_o - C_t} + k_o = \frac{k_1 t}{C_o - C_A t} \quad (2.21)$$

Where, C_o is the surface concentration at time = 0 and C_A is the equilibrium surface concentration at time = t .

2.2.2.2 Adsorption Diffusion Models

Liquid-solid adsorption processes involve film diffusion, intraparticle diffusion, and mass action. Considering physical adsorption, mass action is a very rapid process and can hence be negligible for kinetic study. The kinetic process of adsorption is mostly always controlled by liquid film diffusion or intraparticle diffusion, one of the processes should be the rate limiting step (Meng, 2005). Therefore, adsorption diffusion models are mainly constructed to describe the process of film diffusion and/or intraparticle diffusion.

2.2.2.2.1 Liquid film diffusion model

2.2.2.2.1.1 Linear driving force model

In liquid/solid adsorption systems the rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law. Combining the rate of solute accumulation in a solid particle and the concentration driving force of solute molecules, the linear driving force rate equation is given by:

$$\frac{\partial q}{\partial t} = k_f S_o (C - C_i) \quad (2.22)$$

where C_i and C denote the concentration of solute at the particle/liquid interface and in the bulk of the liquid far from the surface, S_o is the particle surface area per unit particle volume.

2.2.2.2.1.2 Film diffusion model

The mass transfer from the liquid phase to the external surface of the adsorbent is an important step in the adsorption process. The mass flux can be expressed by multiplying the overall rate coefficient by the driving force, which is the concentration gradient between the boundary layers. The film diffusion mass transfer rate equation is given by:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -R' t \quad (2.23)$$

Where:

$$R' = 3 \frac{D_e}{r_o \Delta r_o k'} \quad (2.24)$$

where R' (min^{-1}) is liquid film diffusion constant, D_e (cm^2/min) is effective liquid film diffusion coefficient, r_o (cm) is radius of adsorbent beads, Δr_o (cm) is the thickness of liquid film, and k' is equilibrium constant of adsorption.

The film diffusion mass transfer rate equation has been successfully applied to model several liquid/solid adsorption cases, e.g., phenol adsorption by a polymeric adsorbent NDA-100 under different temperature and initial concentration conditions (Meng, 2005).

2.2.2.2.2 Intra-particle diffusion model

In most liquid-phase adsorption processes, intra-particle diffusion is the rate-determining step in the adsorption process. Intra-particle diffusion is classified into two main types of mechanisms depending upon the method of adsorbate transport, “pore diffusion” and “surface diffusion” (Moon & Lee, 1983).

Various mathematical models on intraparticle diffusion have been proposed (Fritz & Schlunder, 1981; Liapis & Rippin, 1977). For the proper simulation and design of adsorption processes, proper description of intra-particle diffusion is essential. Understanding of diffusion inside macro- and micro-pores, (see Figure 2.9) and differentiating different diffusion mechanisms inside the pores of an adsorbent is vital.

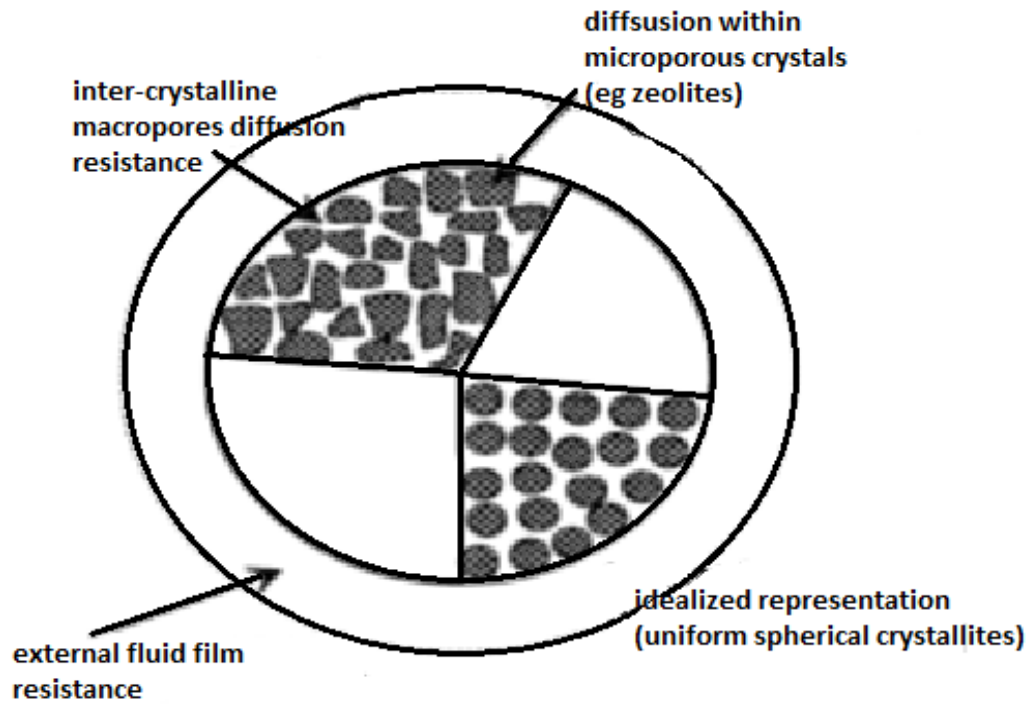


Figure 2.9: Schematic diagram of adsorbent depicting three main diffusion resistances (Krishna, 1993)

2.2.2.2.1 Pore Diffusion Model

The pore phase diffusion model assumes the adsorbent particle as consisting of a solid phase interspersed with very small pores. The adsorbate diffuses into the pores in the fluid phase and adsorption occurs at the internal surfaces. Edeskuty & Amundson, (1952); Kasten & Amundson, (1952) obtained analytical solutions in terms of infinite series for linear adsorption isotherms with batch and fixed-bed reactor configurations. DiGiano & Weber, (1973); Weber & Chakravorti, (1974) used the same approach to study adsorption in finite and infinite bath systems. In the finite bath system, assumption of irreversible immobilization and quasi-steady in the solid phase is made. The latter assumption implies that the rate of immobilization of the solute is rapid compared to the motion of the solution front in the solid. The model is suitable only for solutes satisfying the dual criteria of irreversible adsorption and large solid-to-liquid equilibrium solute distributions. A number of other solutions for the pore model were also developed using the assumption of a linear isotherm (Lapidus & Amundson, 1952; Masamune & Smith, 1964).

Pore diffusion occurs when the adsorbate molecules are transported by the diffusion in the pore fluid and is characterised by the equation:

$$\varepsilon \frac{\partial C}{\partial t} + \rho \frac{\partial q}{\partial t} = \rho \frac{D_{ep}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (2.25)$$

where ρ is the bed density, r_p is the radius of adsorbent pellets, D_{ep} refers to the effective pore diffusion coefficient, and r is the distance to the centre of the pellet.

2.2.2.2.2 Homogenous Solid Diffusion Model (HSDM)

In the homogeneous diffusion model, the particle is considered as a homogeneous net of the adsorbent from the liquid phase to the solid phase work, and the driving force for the adsorbate diffusion can be written as (Tien, 1994):

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (2.26)$$

where D_s is intraparticle diffusion coefficient, r radial position, and q the adsorption quantity of solute in the solid varying with radial position at time t .

HSDM has been applied to different kinds of adsorption systems, such as the adsorption of salicylic acid and 5-sulphosalicylic acid from aqueous solutions by hypercrosslinked polymeric adsorbent NDA-99 and NDA-101. In the adsorption systems of pentachlorophenol (PCP) onto activated carbon, diffusion coefficient D_s evaluated from batch kinetic adsorption experiments has been applied to fixed-bed situation such as the prediction of the adsorption breakthrough curves and design of fixed beds for removal of PCP (Slaney & Bhamidimarri, 1998).

When additional reaction occurs in adsorption process, the conventional HSDM considering only the diffusion mechanism is no longer suitable (diffusion and reaction combined equation). The basic mathematic form of HSDM involved with reaction equation is given by (Tien, 1994):

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) - R_r \quad (2.27)$$

2.2.2.2.3 Pore and Surface Diffusion Model

When the adsorbate molecules diffuse on the surface of the pore wall by the hopping mechanism, the diffusion mechanism is "surface diffusion." Surface diffusion and pore diffusion often proceed in parallel; and they are called "combined diffusion" (Moon & Lee, 1983), and are characterised by the equation:

$$\varepsilon \frac{D_{ep}}{r^2} + \rho \frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) + \rho \frac{D_p}{r^2} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (2.28)$$

Adsorption rates in porous adsorbents are mostly limited by mass transfer within the pores rather than by the kinetics of sorption at the surface, with the exception of biological separations where the kinetics of bond formation have been found to be extremely slow (Levan et al., 1997).

2.2.2.2.4 Weber-Morris model

The intra-particle diffusion model proposed by Weber & Morris has been widely applied in the analysis of adsorption kinetics (Wu et al., 2009). Weber & Morris, (1963) found that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t (Alkan et al., 2007):

$$q_t = k_{int} t^{1/2} \quad (2.29)$$

where k_{int} is the intra-particle diffusion rate constant.

2.2.2.2.5 Double-exponential model (DEM)

Wilczak & Keinath, (1993) proposed a double-exponential function for the adsorption of lead and copper onto activated carbon. The uptake process involved a rapid phase with external

and internal diffusions, and a slow phase controlled by intraparticle diffusion. The two-step mechanism was described fairly well with the double-exponential model (Chiron et al, 2003):

$$q_t = q_e - \frac{D_1}{m_a} \exp(-k_1 t) - \frac{D_2}{m_a} \exp(-k_2 t) \quad (2.30)$$

Where:

D_1 is the adsorption rate parameter for the rapid step (mmol/L);

D_2 is the adsorption rate parameter for the slow step (mmol/L);

k_1 is the diffusion parameter for the rapid step (min^{-1}); and

k_2 is the diffusion parameter for the slow step (min^{-1}).

2.3 Breakthrough Curve

Fixed-bed columns are mostly used in the majority of large-scale applications of adsorption processes although fluidised beds, cyclic beds and expanded beds have also been used. The behaviour of fixed-bed adsorption columns is often illustrated with breakthrough curves, see Figure 2.10 below. Initially, the adsorbent adsorbs the pollutant from the inlet stream readily and efficiently, so that the pollutant concentration of the outlet stream is close to zero. Here, the bulk of the adsorption is taking place near the inlet with the rest of the bed removing the traces. Traces of the adsorbate begin to appear at the outlet and eventually, the inlet region becomes saturated and the main region of adsorption moves towards the outlet. When the outlet concentration begins to rise rapidly, the so-called “break through point” has been reached.

As the fluid flows through the adsorbent material in a packed column, the amount adsorbed comes to equilibrium with the adsorbate influent concentration, in the saturation zone. Thereafter a region with increasing concentration of the adsorbate in which the mass transfer occurs is seen, the mass transfer zone (MTZ), or the shock wave front. The depth of this zone is affected by many variables such as characteristics of the adsorbate and the adsorbent, flow velocities and bed height. It advances to the bottom of the column where the adsorbate concentration in the fluid starts to rise gradually and it eventually turns into exhaustion point and regeneration is required. The breakthrough curve normally takes an S-shape. The

steepness of the breakthrough curve determines the extent to which the capacity of an adsorbent bed can be utilised. Thus, the shape of the curve is very important in determining the length of the adsorption bed. In actual practice, the steepness of the concentration profiles shown previously can increase or decrease, depending on the type of adsorption isotherm involved.

A steep breakthrough curve is more desirable than a flat one. For a steep curve, the bed saturation may reach 80 per cent, but with a flat curve only 15-20 per cent may be typical before breakthrough. The calculation methods for adsorption, particularly in porous adsorbents, must allow for heat and mass transfer to the adsorbed substance in pores. Adsorption process systems with high film transfer coefficients, internal diffusivities and favourable isotherms give steeper sloped breakthrough curves. The dynamic or breakthrough capacity of the bed is crucial for the rationale design of the adsorption process. It provides the basis of a very simple design method, which permits reliable scale-up from small-scale laboratory experiments. In ideal processes, neglecting mass transfer resistance and axial dispersion, the MTZ will have an extremely small width and the breakthrough curve would be a vertical line, ranging from 0 to 1.0 when the entire solid is saturated.

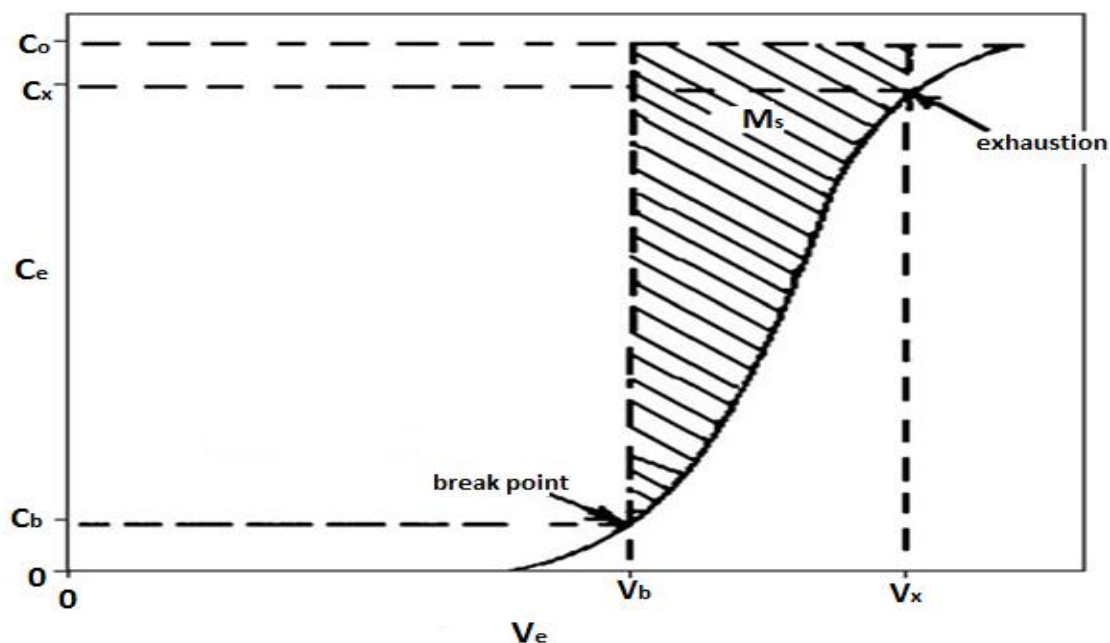


Figure 2.10: Breakthrough curve for the sorption process in fixed beds (Barros et al., 2013)

It should be noted that the effluent contains always some amounts of adsorbate and the theoretical equilibrium concentration is rarely achieved in real situations. The mass transfer resistance and the axial mixing in real systems lead to deviations from the equilibrium theory. In systems with favourable isotherms the shock wave front is replaced by a term called constant pattern behaviour. The concentration profile spreads in the initial region until stable situation is achieved. At this point the mass transfer occurs at the same rate at every point along the wave front. This means that the shape of the mass transfer zone remains unaltered for the majority of the bed.

2.4 Process Modelling, Simulation and Optimisation

A lot of focus and interest has been dedicated to the modelling of kinetic and equilibrium adsorption phenomena for fixed bed adsorbers as an option to shy away from high costs of the experimental set-up for industrial scale-up (Nouh et al., 2010). Mathematical models allow for the study of the kinetics of fixed bed adsorption columns and the breakthrough curves of the adsorption processes (Babu & Gupta, 2005). Various mathematical models have been proposed for liquid adsorption processes based on statistical thermodynamics used for the estimation of the required parameters (Salem & Hamid, 1997) and these include the ones mentioned on in section 2.2.2.

Process models are very useful in plant analysis as they can be used for operator training; safety analysis and the design of safety systems; process design and process control systems designs. The evolution in computer science and development of complex numerical methods has allowed the modelling and solution of processes, while in the past one had to separate the system to its constituent parts. Whereas mathematical modelling deals with quantitative rather than qualitative treatment of the process, optimisation deals with the qualitative selection of the best among the entire set by efficient quantitative methods.

Differential equations can be used to describe nearly all systems undergoing change in science, engineering, economics, social science, biology, business, health care, etc. Models for adsorption processes can be grouped according to the time and space dependency of dependent variables (concentration, temperature e.t.c) (Rodrigues et al., 2012). Considering continuous models for the interstitial flow and/or Fickian representation for particle mass transfer, results in distribution models containing a set of partial differential equations (PDEs) mixed with ordinary differential equations (ODEs). As PDEs obtained in the modelling of

adsorption processes cannot be solved by analytical methods in most cases, numerical solutions are usually deployed. This initially involves reduction of the PDEs into ODEs. Rodrigues et al., 2012 reported two main discretization techniques for the reduction of PDEs, finite differences and weighed residual methods.

The finite difference is the most popular method and here the domain is divided into a set of points where the derivatives are approximated. Many finite difference method have been used in the solving of adsorption models PDEs (Sun & Meunier, 1991; Mashayekhpour & Talaie, 2014). Standard finite difference (Ko et al., 2003) and orthogonal collocation methods (Khashimova, 2013) have been used in the majority of the studies (Brian et al., 1986). The equations give the shape of templates describing parameter values at one node to the values at neighbouring nodes. Simulation is employed in the validation of the process design, the process integrity and operational study of the model. It helps to visualise the process system and trends at various conditions of the existing plant as well as those of a new situation of the plant (Maniar & Deshpande, 1996). It is much easier and cheaper to incorporate actual process data into a simulation model to study the effects on the process, rather than to build a pilot plant (Iglesias & Paniagua, 2006).

The development of computer simulation programs to aid in the design and optimisation of industrial batch stirred-tank and packed-bed column adsorption and chromatography units continues to attract major attention. Various simulation models such as the Monte Carlo simulation model (Khashimova, 2013) and integrated CFD (Computational fluid dynamics) approached (Nouh et al., 2010). Various codes for batch stirred-tank adsorption units designated as TANSIMK, TANSIMA and TANSIMP have also been developed.

2.5 Adsorption Simulators Packages

Simulator packages have wide application areas in process industry. They often come with sophisticated languages and formalisms for model development that allow the description of complex models with differential/ algebraic equations. Many simulation packages are available for modelling commercial processes and these include MATLAB, ASPEN PLUSTM by Aspen Technology Inc., CHEMCADTM by ChemStations, Inc., HYSYSTEM by Hyprotech Ltd., gPROMS by Process Systems Enterprise Ltd. and PRO/II by Simulation Sciences Inc., etc. With the ever-increasing capabilities in computer power and accurate

models for describing process units, process simulators make it possible to do rigorous analyses and exploring different design alternatives. In addition to the classical experimental approaches (e.g. bench scale, mini-plant, pilot plant, market development plant), the use of modelling and simulation tools is becoming increasingly popular and powerful. For the proposed work MATLAB 2010RA will be used for the simulation.

Chapter 3: Modelling of the Adsorptive Desulphurisation of Diesel Fuel on a Polymer Supported Imidation Agent

3.1 Fixed bed adsorption column design

Fixed bed adsorbers have been widely used in the purification of liquid mixtures, in particular process effluents. Fixed bed adsorption columns are fixed vertical beds of porous granular adsorbents, and they can be operated either in series or in parallel. The stream to be treated is injected into the column either by the down flow or the up flow modes. Flow of adsorbing fluid usually is down flow through the bed and that of regenerant usually is upward. The down flow mode has the advantage of allowing for the adsorption of the pollutant and the filtration of suspended solids to be accomplished in a single step. This has resulted in more use of the down flow beds to eliminate the accumulation of particulate material at the bottom of the bed which would require subsequent removal by back washing. Small scale column tests can be used to simulate the behaviour and performance of the adsorbent. Packed bed columns are designed using the scale-up procedure or the kinetic approach and both approaches require a breakthrough curve.

3.1.1 Principles

During an adsorption cycle, the adsorbent at the inlet end of the bed gets saturated and is in equilibrium with the adsorbate in the influent stream. At the exit end, the adsorbate concentration of the adsorbent is still at its initial value. In between the adsorption bed, there is a reasonably well-defined mass-transfer zone in which the adsorbate concentration drops from the inlet to the exit value and this zone progresses through the bed as the run proceeds. To ensure efficient operation of the process, the process must be stopped just before the breakpoint to avoid the effluent concentration rising sharply.

3.1.1.1 The breakthrough concept

Mathematical models are important tools in the design of sorption in fixed bed columns and their validation is often done by experimental data at laboratory scale. Mathematical models are useful for designing and optimizing purposes in industrial scale (Barros et al., 2013). The design of an adsorption column helps to predict the service time until the column effluent exceeds the maximum allowed pollutant concentration. The progress of the mass transfer zone (MTZ) introduces time in the modelling equations which introduce a set of partial differential equations for the mass transfer phenomena and heat transfer phenomena (where applicable). The breakthrough time and the shape of the breakthrough curve are very important characteristics for the determination of the dynamic response of the adsorption column (Gupta & Babu, 2010).

The breakpoint time, t_b is the time at which the effluent concentration reaches its maximum permissible discharge level and is usually considered to be about 1-5% of the inlet solute concentration. In the design of fixed bed adsorbers, several models for mathematical analysis and prediction of the shape of the breakthrough curve have been employed including the Mass-Transfer Zone (MTZ) model, and the Height Equivalent of a Theoretical Plate (HETP) model. The most commonly used data analysis method is the Bed-Depth-Service-Time (BDST) model (Bohart & Adams, 1920). A breakthrough curve and in particular the width of the sorption zone are important characteristics for describing the operation of a fixed bed adsorption column.

3.1.1.2 Empty Bed Residence Time (EBRT) model

The empty bed residence time is the time required for the liquid to fill the empty column and is given by the equation:

$$EBRT = \frac{\text{Bed Volume}}{\text{Volumetric flowrate of the liquid}} \quad (3.1)$$

The adsorbent exhaustion rate is the mass of adsorbent used per volume of liquid treated at break-point time given by:

$$\text{Adsorbent exhaustion rate} = \frac{\text{mass of absorbent in column}}{\text{volume treated at breakthrough}} \quad (3.2)$$

3.1.1.3 Length of Unused Bed

The fraction of unused bed length is given by:

$$L_{unb} = \left(1 - \frac{t_u}{t_t}\right) L \quad (3.3)$$

Where:

t_u is the time equivalent to the usable capacity of the bed

t_t is the time equivalent to total stoichiometric capacity of the packed-bed column

L is the length of the fixed bed

t_u and t_t are calculated from the breakthrough curve by the equations:

$$t_u = \int_0^{t_b} \left(1 - \frac{C}{C_o}\right) dt \quad (3.4)$$

$$t_t = \int_0^{\infty} \left(1 - \frac{C}{C_o}\right) dt \quad (3.5)$$

L_{unb} is assumed to be constant and, as a consequence, is an important element in the scaling-up of processes and represents the mass-transfer zone (MTZ). Small values of L_{unb} imply that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance and that there is no axial dispersion.

3.1.1.4 Bed Depth Service Time Model

The Thomas model is also referred as bed-depth-service-time (BDST) model. The BDST approach is based on the irreversible isotherm model by Bohart & Adams, (1920), and describes the relationship between the service time and bed height for a fixed bed adsorber. This simplified design model ignores the intraparticle (solid) mass transfer resistance and the

external (liquid film) resistance such that the adsorbate is adsorbed onto the solid surface directly. This means that the rate of adsorption is controlled by the surface reaction between adsorbate and the unused capacity of the adsorbent. Also, this model is essentially a constant pattern model. The expression by Thomas for an adsorption column is given as follows:

$$\frac{C_e}{C_o} \cong \frac{1}{1 + \exp \left[\frac{\Theta}{Q} (q_{max}M - C_o V_{tot}) \right]} \quad (3.6)$$

Where: C_e and C_o are the effluent and inlet solute concentrations, q_{max} is the maximum adsorption capacity, M the total mass of the adsorbent, Q is the volumetric flow rate, V_{tot} is the throughput volume and (Θ) is the Thomas rate constant (units in: volume/mass*time).

Compared to diffusion based models which involve the diffusion coefficient or the external mass transfer coefficient, the BDST based models are single parameter models, involving only (Θ) , as q_{max} is an experimentally derived parameter. The determination of L_a is requiring the whole experimental equilibrium curve and in case of sigmoidal or other non-Langmuir or Freundlich-type isotherms these models are non-usable. By this point of view, BDST models are more easily applied in adsorption operations, at least as a first approximation (Vassilis, 2010).

3.2 Mathematical modelling

The determination of the rate-limiting step is an important factor to be considered in the design of adsorption processes. The adsorption (mass transfer mechanism) is usually specified by three consecutive steps:

- (i) mass (adsorbate) transfer from the liquid phase to the solid phase across the external boundary layer film;
- (ii) mass diffusion into the pore or inner surface of the adsorbent; and
- (iii) adsorption on the internal surface of the adsorbent.

The rate-limiting step can be a single step or a combination of steps and the overall mass transfer rate will be controlled by the slowest step.

3.2.1 Basic equations for adsorption column

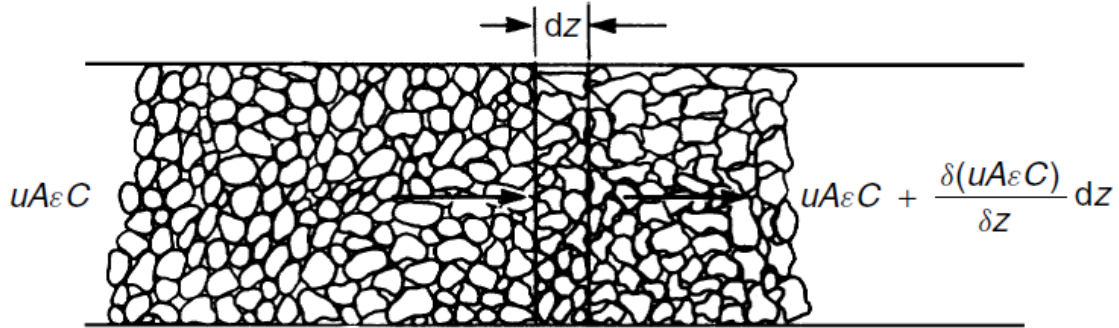


Figure 3.1: Mass balance in element of a fixed bed (Richardson et al., 2002)

At the beginning of the process, the adsorbent is assumed to be fresh, for the entire column length. The effluent is introduced in a downward mode through the column as shown in Figure 3.1. Taking into account both external and internal mass-transfer resistances, the mass balance of the adsorbate in the fluid flowing through an increment dz of the column in Figure 3.1 is given by:

$$\text{Material in} - \text{Material out} = \text{Accumulation} + \text{Loss of adsorption} \quad (3.7)$$

$$uA\varepsilon C - \left[uA\varepsilon C + \frac{\partial(uA\varepsilon C)}{\partial z} dz \right] = \frac{\partial(A\varepsilon C dz)}{\partial t} + \frac{\partial(1 - \varepsilon)AC dz}{\partial t} \quad (3.8)$$

The macroscopic mass conservation equation is given by:

$$-\frac{D_L \partial^2 C}{\partial z^2} + u \left(\frac{\partial C}{\partial z} \right) + C \left(\frac{\partial u}{\partial z} \right) + \left(\frac{\partial C}{\partial t} \right) + \rho_b \frac{(1 - \varepsilon)}{\varepsilon} \left(\frac{\partial q_p}{\partial t} \right) = 0 \quad (3.9)$$

Where:

D_L is the axial dispersion coefficient,

C is the initial sulphur concentration in the fuel,

z is the axial coordinate,

u is the superficial velocity

ε is the bed porosity,

t is the time,

ρ_b is the bed density,

q_p is the adsorption capacity

The following will be assumed for the proposed model:

1. The adsorption process is isothermal. This assumption implies the adsorption parameters and adsorption equilibrium coefficients are constant.
2. The equilibrium of adsorption is described by the theoretical Freundlich isotherm.
3. The concentration gradients in both the radial and longitudinal directions are negligible. For a bed/pellet diameter ratio of greater than 20, channelling at the wall and random variation in the interstitial velocity within the bed are negligible (Richardson et al., 2002).
4. There is no axial dispersion in the column $\left[\frac{D_L \partial^2 C}{\partial z^2} = 0 \right]$, implying uniform flow or plug flow.
5. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, k_f .
6. The linear velocity of the liquid phase does not vary along the column.
7. Single solute adsorption process is assumed.

Taking into account the above assumptions, Equation 3.3 reduces to:

$$u \left(\frac{\partial C}{\partial z} \right) + \left(\frac{\partial C}{\partial t} \right) + \rho_p \frac{(1 - \varepsilon)}{\varepsilon} \left(\frac{\partial q_p}{\partial t} \right) = 0 \quad (3.10)$$

With the initial and boundary conditions:

$$C = 0 \quad \text{and} \quad q_p = 0 \quad 0 < z < H \quad (3.11)$$

$$C = C_o \quad \text{for} \quad z = 0 \quad t > 0 \quad (3.12)$$

Equation (3.12) shows that at lengths greater than H , there is no solute transfer due to unavailability of sorbent material as there is no adsorption capacity.

The adsorption equilibrium is described by the Freundlich isotherm, based on the calculation from the adsorption data. As already discussed in 2.2.1.2, the Freundlich isotherm does not have much limitation as it can fit both homogeneous and heterogeneous surfaces, and both physical and chemical adsorption and has been successfully applied in adsorption behaviours for organic compounds and reactive matters. Also the data reported by Fadhel, (2010a) fit the Freundlich model better. The Freundlich equation is given by:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3.13)$$

Where q_e is the concentration of solute adsorbed by the adsorbent, K_F is an indicator of adsorption capacity, n is a constant related to the adsorption intensity and C_e is the concentration of the solute in solution.

The adsorption kinetics of sulphur compounds is controlled by the liquid phase solute transfer and the subsequent adsorption of the sulphur:

1. Liquid phase solute transfer - diffusion of sulphur compounds from the boundary film to the surface of the sorbent:

The transport of the adsorbate from the bulk of the solution to the external surface of the adsorbent is an important step in the overall uptake process of sulphur. Considering porous film diffusion, the interphase mass transfer rate expressed in terms of the boundary film flux is given by;

$$\frac{\partial q_p}{\partial t} = \frac{3k_f}{a_p \rho_s} (C - C_e) \quad (3.14)$$

Where a_p , is the radius of the adsorbent particles, ρ_s is the solution density and k_f is the external film transfer coefficient.

2. Diffusion of the sulphur compounds from the surface to the pores active sites;

From Mužic et al., (2010a) and Mužic et al., (2010c) experiments, the reaction rate of sulphur compounds adsorption from diesel fuel was found to be excellently described by the pseudo second order equation given by the equation :

$$\frac{\partial q}{\partial t} = k_2 (q_e - q_t)^2 \quad (3.15)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively and k_2 is the pseudo-second-order rate constant for the kinetic model.

Introducing boundary equations:

$$q_t = 0 \quad t = 0 \quad (3.16)$$

$$q_t = t \quad t = t \quad (3.17)$$

and integrating gives (Ho, 2004) :

$$\log(q_e - q_t) = \log q_e - \frac{k_2}{2.303} t \quad (3.18)$$

3.2.2 Simulation Technique

Equations (3.10), (3.13), (3.14) and (3.15) were solved numerically using the MATLAB (Appendix C). The partial differential equations were first reduced to linear ordinary differential equations using the Backward Time Difference and Central Difference (Implicit numerical solution) in approximating the spatial derivative. This finite difference method was chosen due to its stability and the nature of boundary condition which is Neumann (Yusuff et al., 2013). In addition to the method being a popular one, the method also has an advantage of having no restrictions on the time-step which is ideal when considering simulation problems. The implicit scheme for the PDE (3.10) is first order in both space and time and is stable for specific time steps.

3.2.3 Parameters for simulation

The properties of the polymer supported imidation agent are given in Table 4.

Table 4: Properties of the PI agent and the equilibrium parameters

Properties of the polymer supported imidation agent (sodium N-chloro-polystyrene sulphonamide)

Effective diameter (μm)	1.9 (Maddah & Azimi, 2012)
Particle radius a_p (μm)	0.95
BET surface area (m^2/g)	34.02
Bulk density ρ_s (g/cm^3)	0.6994
Freundlich constants	
K_F (mg/L)	0.362
n	0.226

The properties of the adsorbent were taken from Fadhel, (2010a) and the isotherm constants calculated from there.

The parameters for the simulation program are given in Table 3.2 below.

Table 5: Model parameters for the simulation

Porosity of the bed, ε		0.58
Particle density, ρ_p	kg/m^3	1000
Adsorption capacity, q_p	mg/g	86.1
External mass transfer coefficient, k_f	m/s	$1.738 * 10^{-2}$
Column length, z	m	0,284
Bed density, ρ_b	kg/m^3	810
Initial sulphur concentration, C_o	ppm	1900
Final sulphur concentration, C_f	ppm	178

With the exception of the external mass transfer coefficient, that was calculated (see Appendix B), all other parameters were based on reported adsorption column specification by (Babu & Gupta, 2005).

3.3 Simulation results

The simulation model was run for 10 hours, treating diesel fuel with 1900 ppm sulphur content. Various parameters were varied to study the simulation model: bed height, bed voidage and initial effluent concentration. The breakthrough curve for the model is shown in Figure 3.2. A sharp front of the breakthrough curve is initially observed, followed by broadening of tail of the breakthrough curve. This trend agrees well with the theoretical phenomena occurring in the adsorption processes. As can be seen in the graph exhaustion of the bed happened after about 10 hours. The simulations are carried out using the present model to carry out a systematic parametric study. The time to breakthrough, that is the time corresponding to about 0.05 of the concentration, is 0.4 hrs and the time to exhaustion of the adsorption bed is about 9 hours.

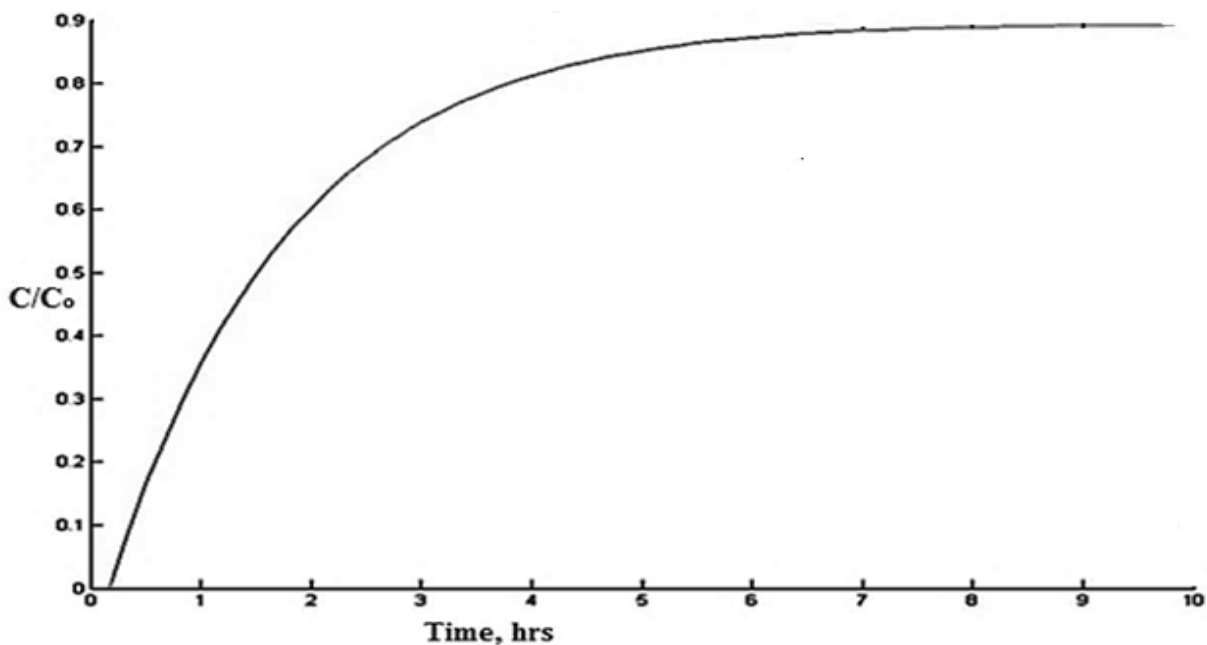


Figure 3.2: Breakthrough curve for the adsorption of sulphur on PI agent

3.3.1 Analytical solutions for breakthrough curve

The effect of the inlet sulphur concentration, adsorption column bed height and the adsorbent particle size were studied.

3.3.1.1 Effect of Inlet concentration

The effect of the inlet sulphur concentration on the breakthrough curves at a bed height of 0.284m and 0.95 μ m is shown in Figure 3.3. The inlet concentration is varied between 500 and 2500 ppm. As the inlet concentration is increased the breakthrough time decreases. Higher inlet concentrations give steeper breakthrough curves and the breakthrough volume is decreased. This is as a result of the lower mass transfer flux due to weaker driving forces. At higher concentrations, there is a higher uptake of sulphur due to more available adsorption sites on the adsorbent, although the breakthrough time is shorter than the breakthrough time at lower concentrations. The breakthrough time for an inlet concentration of 500 ppm is 0.25 hours and 0.2 hours for 2500 ppm inlet concentration. As the inlet concentration increases, the time to saturation of the adsorption bed increases. This means less cycles to regeneration.

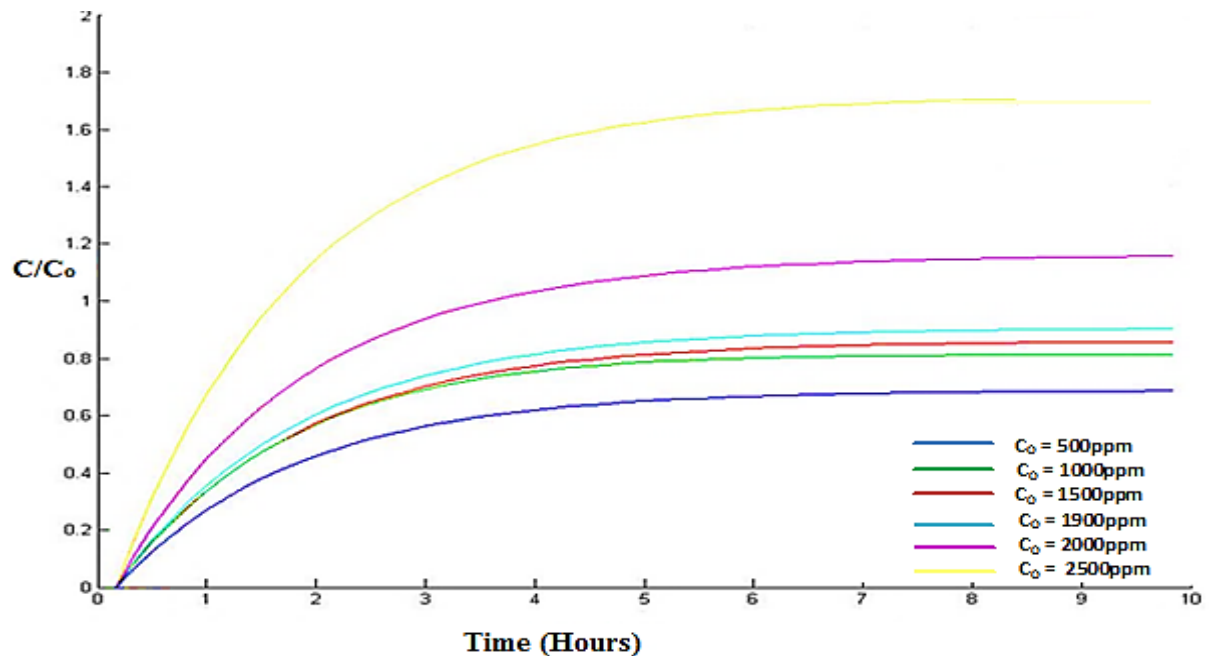


Figure 3.3: Effect of inlet concentration on the breakthrough curve

3.3.1.2 Effect of bed height

Breakthrough curves for the adsorption of sulphur compounds on the polymer supported imidation agent at various bed heights (between 0.25m and 0.35m) with an inlet concentration of 1900ppm and particle radius of 0.95 μ m are shown in Figure 3.4.

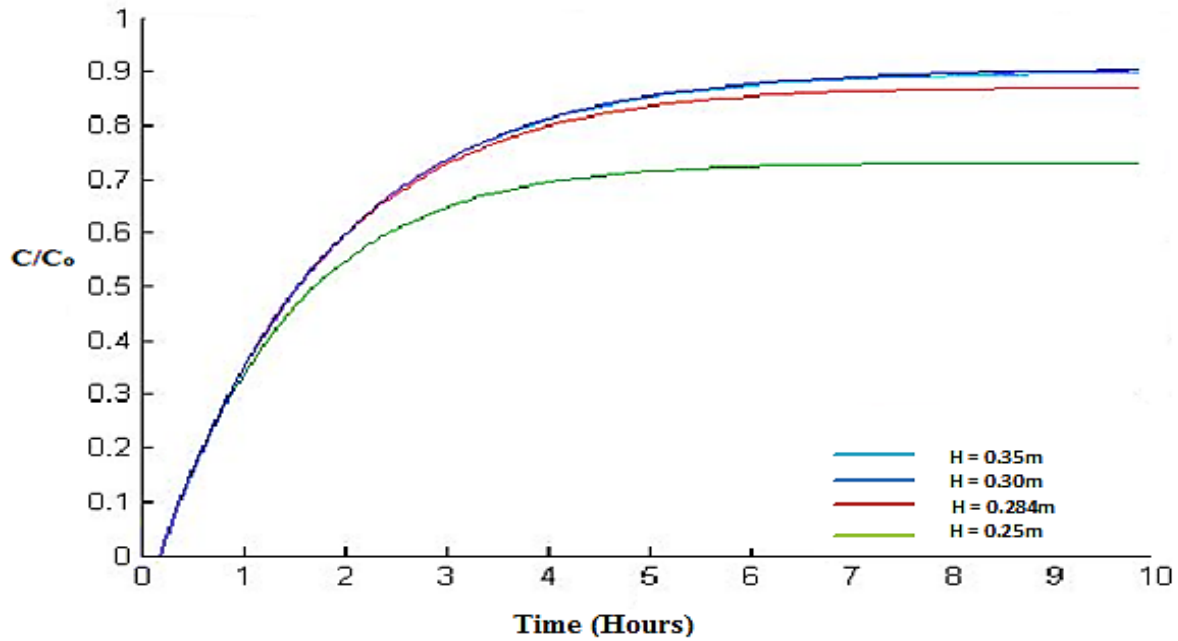


Figure 3.4: Effect of bed height on the breakthrough curve

As the height of the adsorption bed is increased from 0.25 to 0.35, the breakthrough time decreases. For smaller bed heights, the bed is saturated in less time. At higher bed heights, the effluent/adsorbate concentration ratio increases rapidly in comparison to smaller bed heights. This means a higher adsorption capacity of the bed is attained due to the increased residence in the column and an increase in the rate of adsorption. Smaller bed height corresponds to less amount of adsorbent than higher bed heights. Between 0.3 and 0.35, the change in the breakthrough curve is not significant with respect to the increase in bed height. As the separation factor for the pollutant to be removed approaches 1.0, a relatively small mass transfer zone is created and an increase in the bed height of the column at the same flow rate will not change the adsorption capacity.

3.3.1.3 Effect of the particle radius

The effect of the particle size (radius) on the breakthrough curves at an inlet concentration of 1900ppm and a bed height of 0.284m is shown in Figure 3.5. Adsorbent particle radii of 0.0005, 0.00095, 0.015, 0.05 and 0.3 mm were studied. As the particle size decreases the breakthrough curve gets steeper. The smaller the particle size, the faster is the kinetic

equilibrium for the process and the higher the breakthrough capacity. This means faster cycle times for the adsorption process. As the particle radius increases, the thickness of the stagnant film around the particles increases and the overall kinetics is reduced. This is because more time is required for the adsorbent particles to reach the adsorption site is required.

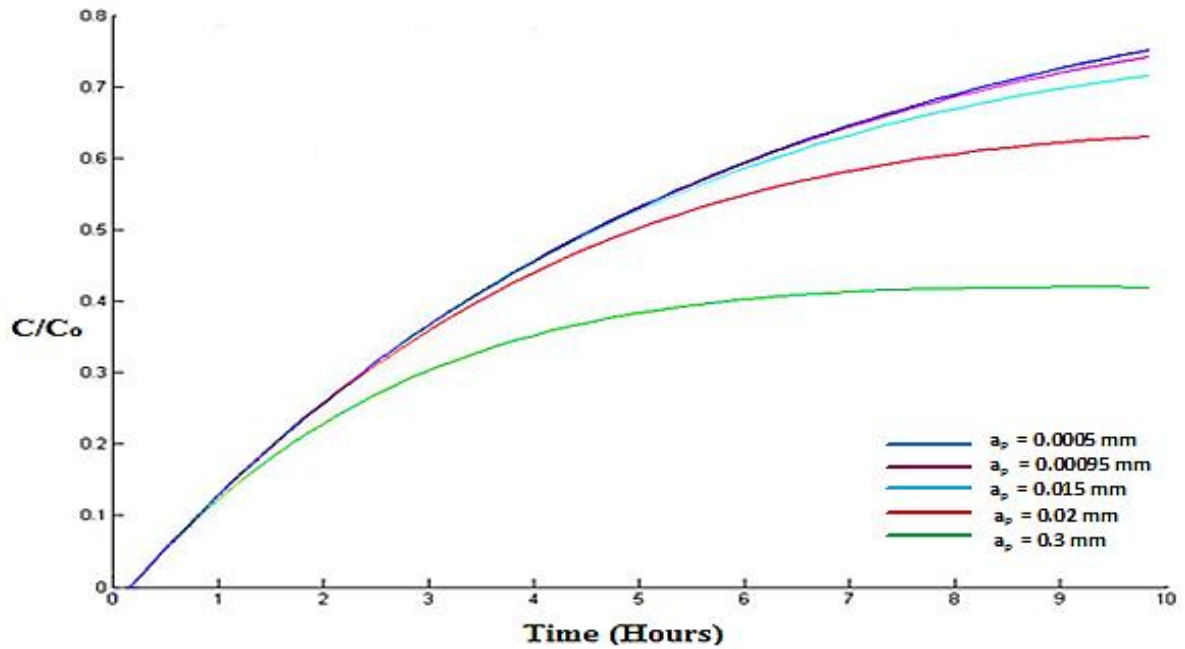


Figure 3.5: Effect of particle radius on the breakthrough curve

With the much lower adsorption particle radii, the time to saturation of the bed becomes much higher and this will be uneconomical. Hence there should be a balance to ensure an economical regeneration time.

Chapter 4: Validation of the proposed simulation model

4.1 Experimental Data

Experiments were carried out to validate the proposed simulation model by varying the inlet sulphur concentration, the bed height and the adsorbent's particle radius. Sodium N-chloropolystyrene sulphonamide was used as the adsorbent in the fixed-bed experiments and had the same properties as listed in Table 4. The polymer was prepared using the same method as reported by Fadhel, (2010b) and the resultant polymer obtained was a light yellow powder.

Fixed-bed experiments using the polymer supported imidation agent with varying inlet concentrations 500 ppm, 1900 ppm and 2000 ppm were carried out in a 30 cm long glass column with an internal diameter of 3 cm and an adjustable flow adapter to hold the packed bed in place. Water was passed through the column at a flow rate of 0.006 mL/min for an hour to remove air bubbles and to flush the adsorbent particles. Adsorption experiments were performed with a flow rate of 0.006 mL/min, influent sulphur concentration of 1900 ppm, 1500 ppm and 500 ppm; bed heights of 20.0 cm and 28.4 cm and 0.02mm and 0.005mm adsorbent particle radius.

4.2 Comparison of experimental data with Simulation

Model validation depends on the ability of a given model to predict a given set of conditions rather than to fit a given condition (Firouztale et al.,1994). This constitutes the validity of the test of the accuracy of the model, its assumptions and the estimated parameter values.

4.2.1 Effect of Initial Sulphur Concentration

The initial sulphur concentration in the experiments was varied and the results are shown in Figure 4.1.

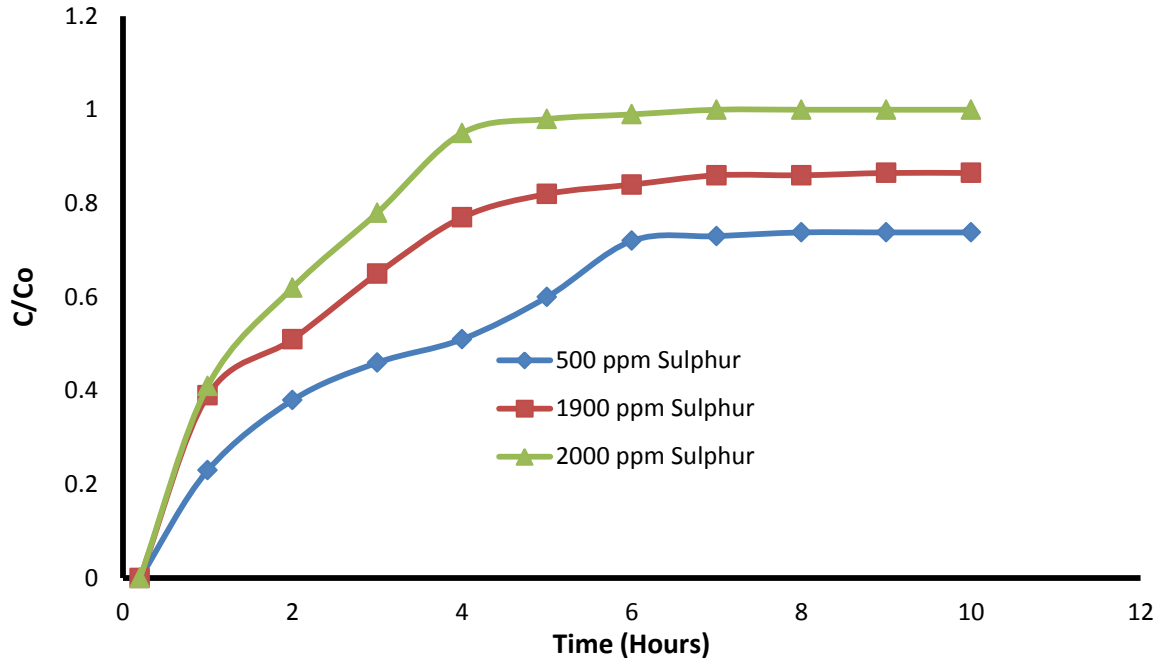


Figure 4.1: Effect of the variation of sulphur inlet concentration - Experimental

As can be seen from the graph, the higher the concentration of the sulphur content the shorter the breakthrough curve. This is the same trend obtained in the simulation results presented in Chapter 3.

Figure 4.2, shows the comparison between the experimental data and the simulation results for the varied inlet sulphur concentration. As can be seen the model predicts the experimental results for the varied concentration well. The experimental breakthrough curves show a slight characteristic displacement effect and this may be attributed to variations in the temperature conditions, non-plug flow characteristics and changes in velocity along the column. To simplify the model, isothermal conditions, plug flow characteristics and constant velocity along the column were assumed and this might vary at certain points within the process.

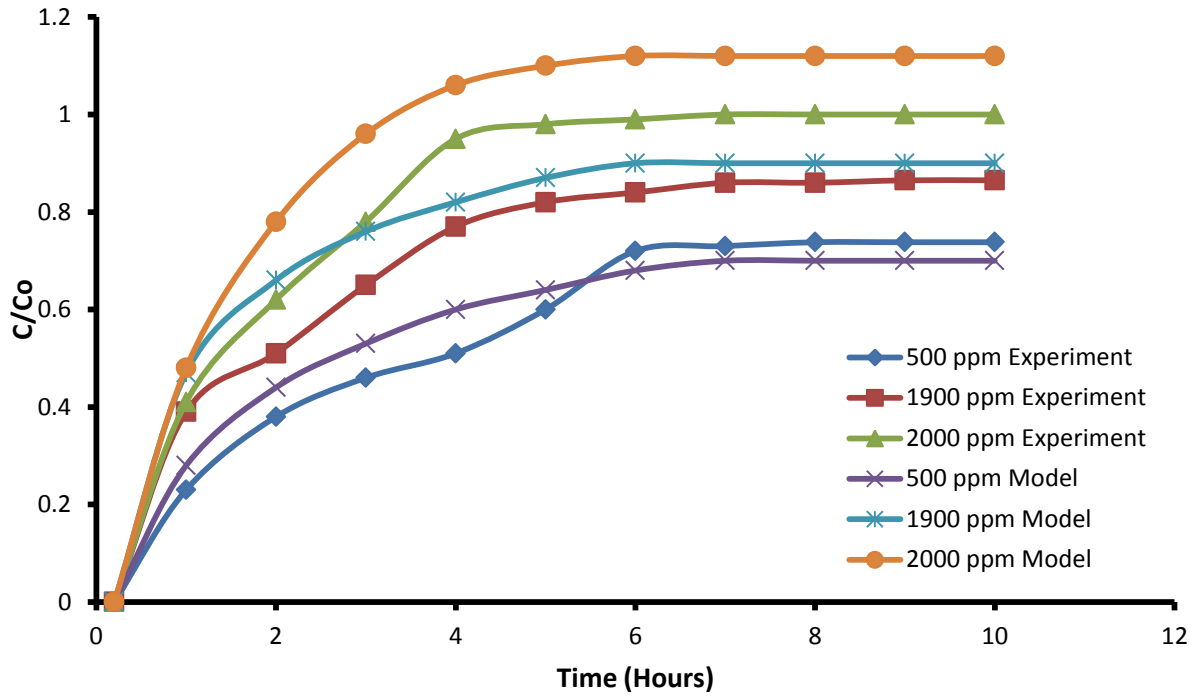


Figure 4.2: Validation of simulation on effect of concentration on the breakthrough curves

4.2.2 Effect of Bed Height

Scaling down the bed height the effect of 28.4 cm and 20.0 cm bed heights was analysed using experiments and the results are shown in Figure 4.3.

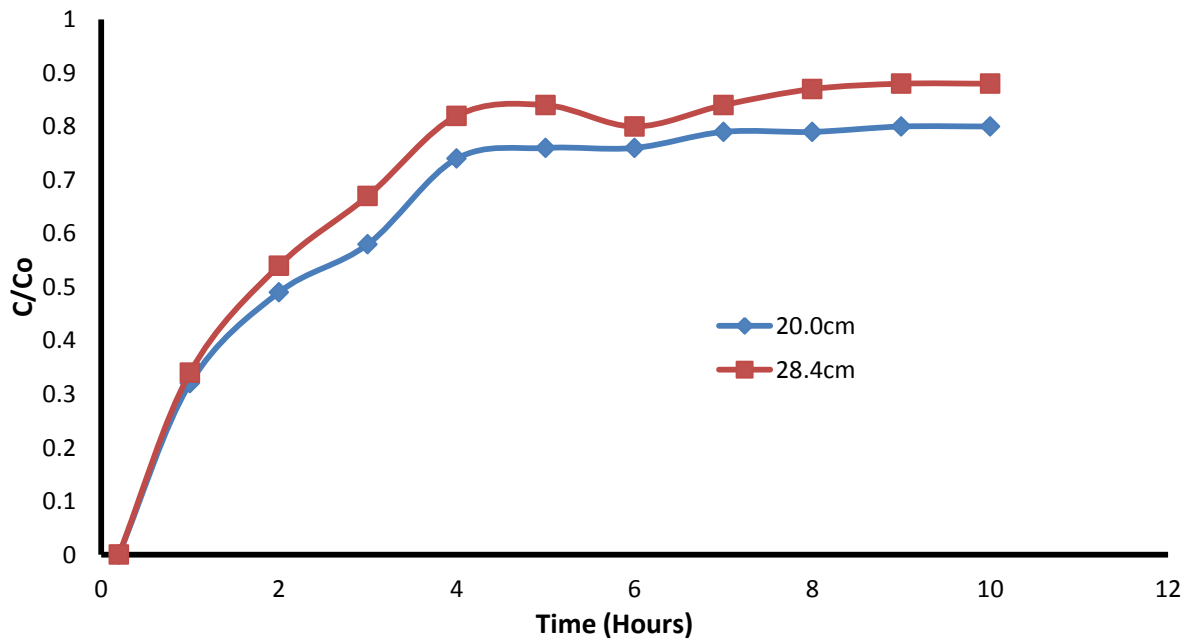


Figure 4.3: Effect of the variation of bed height – Experimental

As clearly shown increasing the bed height of the column within the specified limits increases the adsorption capacity of the adsorbent, the same trend reported in the simulation results in Chapter 3.

Comparison of the bed heights used in the experiments and the bed heights used in the simulation model after scaling gives Figure 4.4.

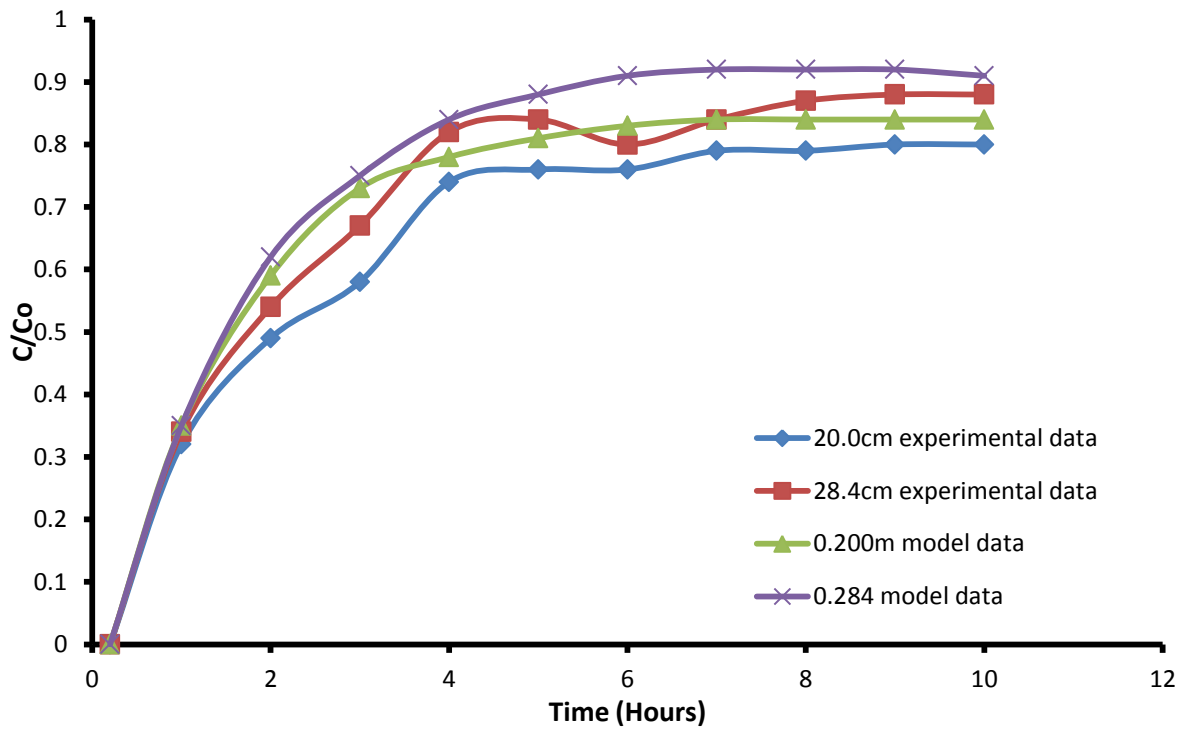


Figure 4.4: Validation of simulation results on effect of bed height on the breakthrough curves

The model simulation results predict the experimental data well. The slight shift between the two is due model assumptions such as isothermal conditions, plug flow characteristics and constant velocity along the column which might vary at certain points within the process.

4.2.3 Effect of Particle Radius

The effect of the adsorbent's particle radius on the breakthrough curve is shown in Figure 4.5.

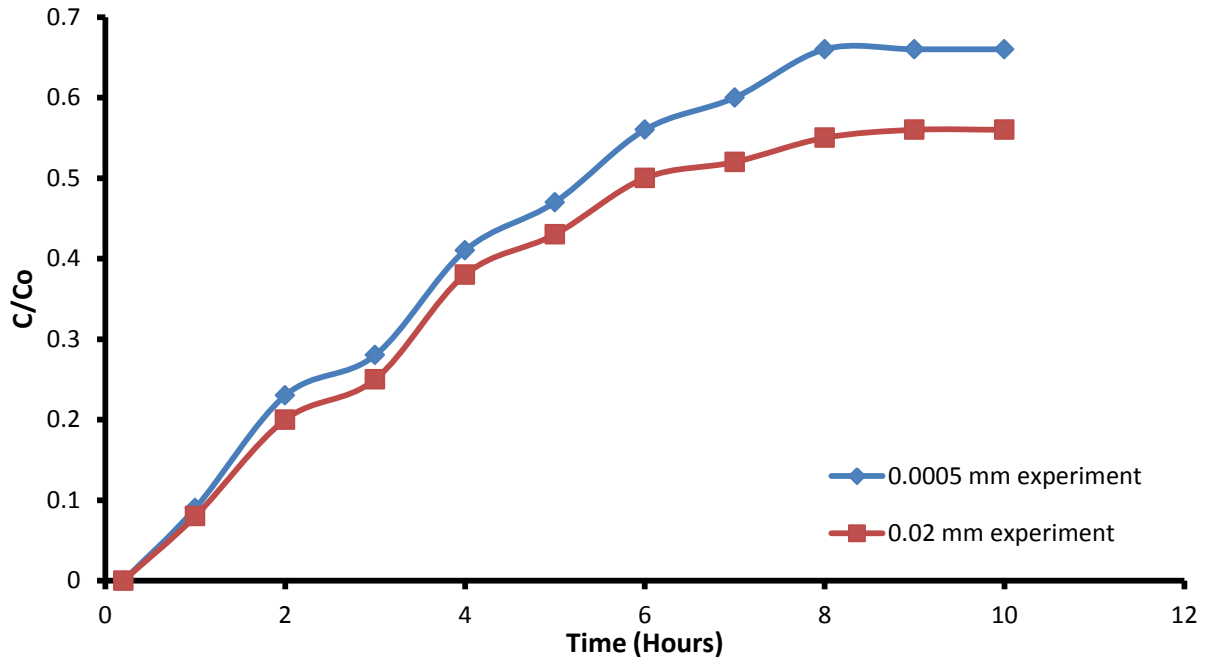


Figure 4.5: Effect of the adsorbent's particle radius – Experimental

As the particle size decreases the breakthrough time also decreases as reported by the simulation model. The comparison of the simulation results and experimental data are shown in Figure 4.6. The experimental data predicts the model well.

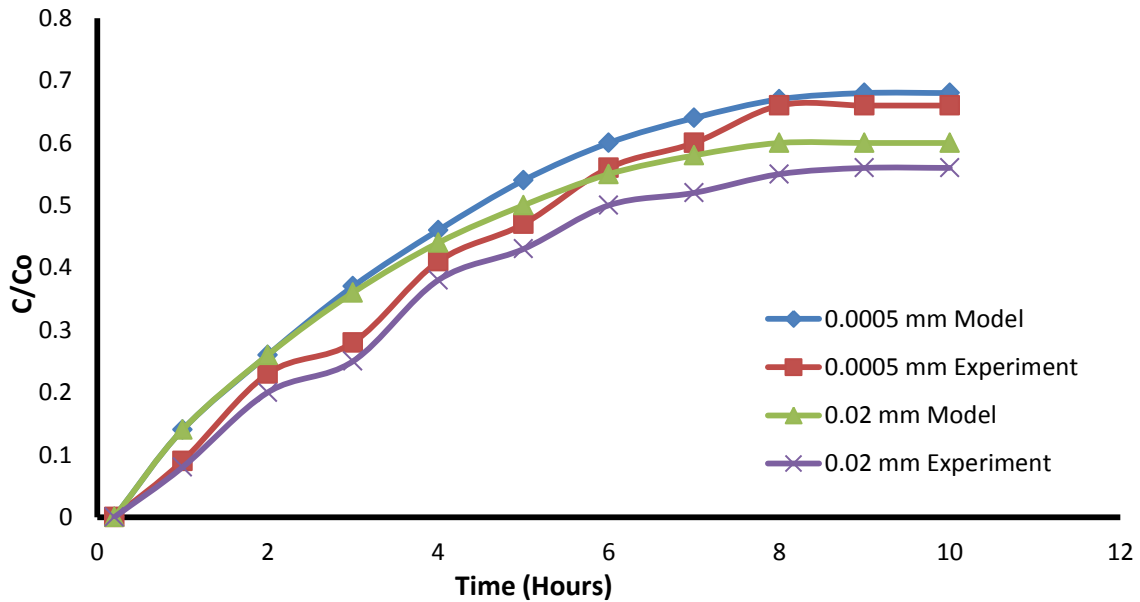


Figure 4.6: Validation of simulation results on effect of adsorbent's particle radius on the breakthrough curves

4.3 Parametric Sensitivity

For the quantification of the sensitivity of the model predictions in relation to the estimated parameters, a sensitivity analysis was carried out. Sensitivity analysis allows the evaluation of models, to determine which input parameters have the highest effect on the predicted output variables. A sensitivity analysis was performed on the three studied parameters; diesel fuel influent concentration, the adsorption column height and the particle radius to observe the overall effect of each parameter to the column system within $\pm 15\%$ parameter perturbation range.

In quantifying the parameter perturbation, the process efficiency for the parameters was calculated and compared to the nominal value. The process efficiency for the adsorption process is given by equation 4.1 below:

$$\varphi_{90\%} = \frac{\left((0.9(t_{C/C_0=0.9}) - \int_0^{t_{C/C_0=0.9}} C/C_0 dt) \right) 100}{0.9(t_{C/C_0=0.9})} \quad (4.1)$$

For the values of $C_0 = 1900$, $H = 0.284\text{m}$ and $a_p = 0.95\mu\text{m}$; the nominal process efficiency was calculated and gave the value of 98.78%.

For the parameters studied; the bed height, the initial sulphur concentration and the particle radius, the parametric sensitivity is shown in Table 6 below.

Table 6: Parametric sensitivity of the model parameters

Parameter	$\varphi_{90\%}(\%)$	
	-15%	+15%
C_0	99.35	98.68
H	98.90	98.82
a_p	95.95	98.67

The most sensitive variable in the process was the particle size, as it varied the most from the nominal calculated value. The percent sensitivity was also determined by dividing the change in the $\pm 15\%$ variation in each of the parameters studied by the total change in the

concentration profile for $\pm 15\%$ variation in the three parameters, and the particle size gave the highest deviation of 78.4%.

Chapter 5: Conclusions and recommendations

5.1 Conclusions

As a result of the strict limits allowable for sulphur emissions, due to their undesirable effects in their combustion, various techniques and methods for desulphurisation are progressively being researched. As adsorption has been evaluated as one of the most cost-effective desulphurisation technology for transport fuels, a lot of research and interest has focused on this technology. This research has focused on the adsorptive desulphurisation of diesel fuel using a polymer supported imidation agent (sodium N-chloro-polystyrene sulphonamide).

A general model for the adsorption of sulphur using a polymer supported imidation agent was developed and the model took into account the mass transfer resistance and pseudo second order reaction model for the adsorption of the sulphur. The model was solved to get the breakthrough curve for sulphur adsorption on the polymer supported adsorbent. The adsorbent was found to be a potentially cost-effective and alternative method for sulphur removal from diesel fuel, despite its slightly low performance. The time to attain equilibrium for the process is 10 hours.

A simulation study of the proposed process was also carried out. The adsorption of the sulphur on the polymer supported imidation agent was found to be dependent on the initial influent concentration, bed depth and the particle radius. Higher influent sulphur concentrations give steeper breakthrough curves and a lower break point time. A bigger bed height increases the adsorbate/adsorbent concentration ratio and hence the adsorption process. A decrease in the particle size reduces the breakthrough time. Beyond 0.35 m for the bed height and 0.00095 mm particle size, there was not much change in the breakthrough curve. The simulation results were validated by an experimental study of the process. In addition, sensitivity analysis on the three parameters was carried out to determine the significance of each process parameter, leading to optimisation of process efficiency.

In addition to giving more information on the feasibility of the polymer supported agent in sulphur adsorption, the research improves the understanding of the adsorption process with more focus on adsorption reaction modelling and simulation.

5.2 Recommendations for future studies

The polymer supported agent has been proposed as a suitable adsorbent for the desulphurisation of diesel fuel. To ensure more accuracy of the developed model, pilot studies of a continuous adsorption process should be carried out. This will confirm the adsorption kinetics better fitted to the process and hence provide more accurate simulation results from the simulation model.

- A modification of the adsorbent to improve its adsorption capabilities is also proposed. This will ensure a more favourable breakthrough curve indicating high adsorption rates. Such modification could be the addition of catalysts.
- Given the effect of temperature on adsorption, future studies need to include the thermodynamic studies of the proposed process.
- As adsorption beds typically include recycle and regeneration, simulation on the process taking both into account would be greatly beneficial.

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Appendix A

Desulphurisation of diesel fuel - model data

A. Isotherm data

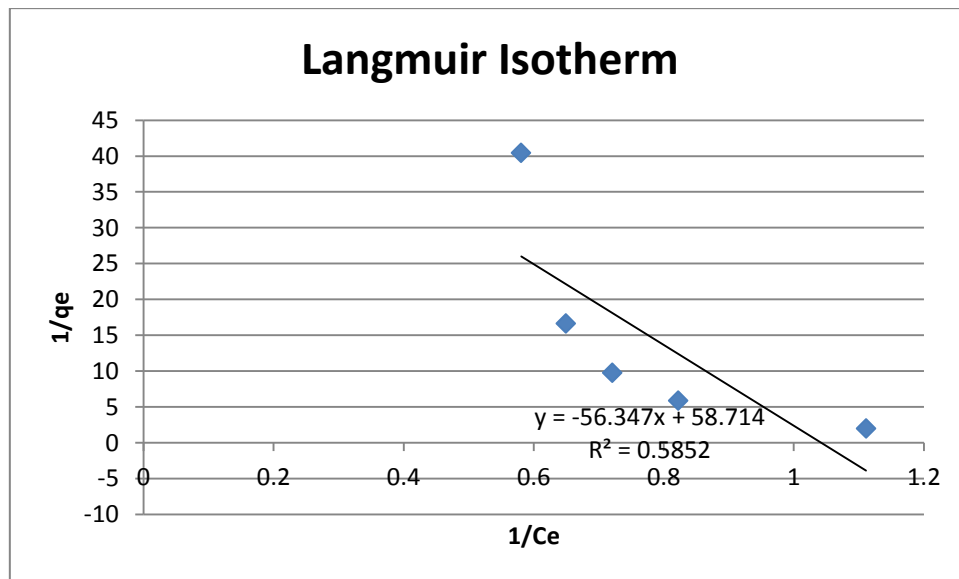


Figure A.1: Langmuir model isotherm data

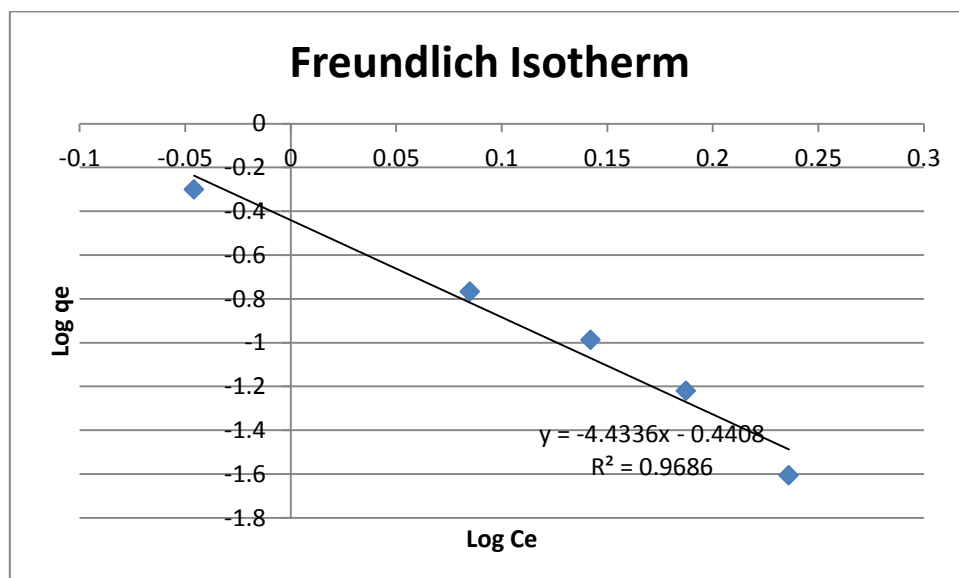


Figure A.2: Freundlich model isotherm data

Appendix B

Calculation of the external mass transfer coefficient

The mass transfer coefficient can be calculated from empirical correlation reported in literature. Wakao & Funazkri, 1987 reported that for the range $3 < Re < 104$:

$$Sh = \frac{k_f d_p}{D_{AB}} = 2.0 + 1.1 Re^{0.6} Sc^{1/3} \quad (B.1)$$

Where: k_f is the mass transfer coefficient,

d_p is the diameter of the particle,

D_{AB} is the mass diffusivity and

Re and Sc are the Reynold's and Schimdt numbers respectively.

$$Re = \frac{\rho d_p u}{\mu} = \frac{d_p U}{\nu} \quad (B.2)$$

$$Sc = \frac{\nu}{D_{AB}} \quad (B.3)$$

For diesel fuel: $D_{AB} = 9.37 * 10^{-9}$; $\nu = 3.98 * 10^{-6}$; $U = 0.1$

Calculating gives:

$$k_f = 1.738 * 10^{-2} m/s$$

Appendix C

Mathematical Code in Matlab

```
clc
clear all
format short
% Parameters to define the advection equation and the range in space and
% time
Hmax = 284; % Maximum length
Tmax = 20; % Maximum time(hrs)
u = 0.1;% Advection velocity
rho_p=10;
eps=0.58;
kf=1.738*10^(-2);
ap=0.95;
Ce=1722;
Co=1900;
Cf=178;
ps=0.6994;
% Parameters needed to solve the equation within the explicit method
m = 40; % Number of time steps
dt = Tmax/m;
n = 10; % Number of space steps
dz = Hmax/n;
alpha = u*dt/(2*dz);
beta=dt*rho_p*(1-eps)*(3*kf)/(eps*ap*ps);
beta
alpha
% Initial value of the function C
```

```

for i = 1:n+1
C(i,1)=Co;
%C(i,m+1)=Cf;
z(i) =(i-1)*dz;
end

% Value of the amplitude at the boundary
for k=1:m+1
C(1,k) = 0;
C(n+1,k) = Cf;
time(k) = (k-1)*dt;

end

% Implementation of the explicit method
for k=2:m % Time loop
    for i=2:n% Space loop
        C(i,k+1)=(1-beta)*C(i,k)-alpha*(C(i+1,k+1)-C(i-1,k+1))+beta*Ce;
    end
end

%figure(1)
%set(gcf,'renderer','zbuffer');
%set(gcf,'renderer','painters');
%mesh(z,time,C')
%title('solute transfer due to availability of sorbent material')
%xlabel('t')
%ylabel('z')

% Graphical representations of the evolution of the wave
%figure(2)
%hold on
%plot(z,C,'r+')

```

```
%hold off
```

```
%figure(4)
```

```
%set(gcf,'renderer','zbuffer');
```

```
%surf(z,time,C')
```

```
%title('solute transfer due to availability of sorbent material')
```

```
%xlabel('t')
```

```
%ylabel('z')
```

```
%figure(5)
```

```
%set(gcf,'renderer','zbuffer');
```

```
%plot(time,C')
```

```
%title('solute transfer due to availability of sorbent material')
```

```
%xlabel('t')
```

```
%ylabel('C')
```

```
figure(6)
```

```
set(gcf,'renderer','zbuffer');
```

```
plot(time,C/Co)
```

```
title('Break Through Curve')
```

```
xlabel('t')
```

```
ylabel('C/Co')
```

```
figure(7)
```

```
set(gcf,'renderer','painters');
```

```
surf(z,time,C')
```

```
title('C(z,t)')
```

```
xlabel('Length z')
```

```
ylabel('Time t')
```