Abstract

Diesel is one of the most commonly used fuels, especially in the transport industry all over the world. During direct combustion of diesel, organic sulfur compounds are converted into $SO_{x.}$ SO_x that form acid rain which cause damages to building, and loss of forests, resulting into destruction of ecosystem when it reacts with vapour in the atmosphere. Furthermore, the release of sulfur compounds into the atmosphere has resulted into health problems such as asthma, lung and heart disease and triggering of heart attack. Therefore, many countries have implemented regulations to refineries around the world to find a way of minimizing the emission of sulfur oxides into the environment. Currently, there is a stringent regulation that refineries in South Africa are expected to ensure a maximum specification of less than 5 ppm sulfur content in the petroleum distillates to levels equivalent to the Euro 5 emission standard by 2020. Therefore, there is a need to look for a better way of desulfurizing South African petroleum distillates to meet up with the stringent policies regarding emission of sulfur oxides. Research focus has been channeled towards hydrodesulfurization (HDS), adsorption (AD), biodesulfurization (BDS), oxidation and extraction. In addition, studies that will explore the combination of BDS with existing method e.g Adsorptive desulfurization (ADS) could be instrumental to achieving a higher reduction in sulfur-containing compounds in the petroleum distillates. In order to contribute to this research line, this study has focused on development and evaluation of adsorption coupling biodesulfurization (AD/BDS) process for the removal of sulfur-containing compounds from South African petroleum distillates.

The adsorbents (pomegranate and neem leaf powder) employed in the adsorptive desulfurization were successfully synthesized by activating with H_2SO_4 and then calcined at 500 ^oC. Carbon nanotubes were purified using HCl and acetic acid then functionalized using $KMnO_4$ and H_2SO_4. Activated carbon was used as-received for batch mode adsorption process, while it was immobilized with sodium alginate for use in continuous packed-bed adsorption experiments, so as to reduce clogging, pressure drop and increase adsorbent loading in the column.

The adsorbents were characterized using Fourier transform infrared (FTIR), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX), X-ray diffraction (XRD), and Raman spectroscopy for surface chemical functionalities, textural

property, morphological structure, chemical composition and structural and chemical information, respectively.

The adsorptive desulfurization experiments were carried out using a model diesel first and real diesel obtained from a typical refinery in South Africa. The model diesel was prepared by dissolving dibenzothiophene (DBT) in hexane. The desulfurized model diesel was analyzed using high performance liquid chromatography (HPLC) and gas chromatography/mass spectrometer (GC/MS). The adsorption performance of each adsorbent was evaluated in a batch mode and a continuous mode. Thereafter, the best adsorbent and operating parameters were used in AD/BDS coupling process. The mechanisms and the kinetic studies of the adsorption process were studied.

Biodesulfurization experiment was performed in a batch mode using growing and resting cells of *Pseudomonas aeruginosa* and *Pseudomonas putida* as biocatalysts. Model diesel used for biodesulfurization experiment was prepared by dissolving dibenzothiophene (DBT) in dimethylformamide (DMF). In addition, two different real South African diesel samples (diesel obtained before HDS (5200 mg/L) and diesel obtained after HDS (120 mg/L) were also used in this study. The best *Pseudomonas* strain, with highest desulfurization efficiency and best operating parameters were then used for the AD/BDS coupling process. The kinetic studies of the bacteria growth and diesel degradation were investigated as well.

In the AD/BDS experiment, real diesel was first transferred to a bed column packed with immobilized activated carbon as adsorbent, and then the desulfurized diesel obtained from the column was transferred into the bacteria basal medium consisting of resting cells of *Pseudomonas aeruginosa* for complete degradation. The desulfurized and the degraded diesel were analyzed using GC/MS. The adsorption performance of the packed-bed column and the degradation efficiency of *Pseudomonas aeruginosa* were evaluated. The kinetics of the AD/BDS process were studied

This dissertation has reported the adsorption performance evaluations of neem leaf powder (NLP) and pomegranate leaf powder (PLP), carbon nanotubes (CNTs), functionalized carbon nanotubes (FCNT) and activated carbon (AC) as promising adsorbents for removal of DBT from model diesel. The dissertation also reports for the first time in open literature the excellent percentage

DBT removal of PLP adsorbent and its adsorption mechanisms. The results show that PLP out-performed NLP by 9.88 %. PLP displayed 70.55 % percentage DBT removal and NLP displayed 65.78 % DBT removal.

As far as it can be ascertained, no study has been conducted on the use of $KMnO_4$/ H_2SO_4 treated-CNTs for removal of DBT from petroleum distillate. It can be concluded that the acid treatment of CNTs enhanced its surface affinity for DBT, thus contributed to the improved adsorption capacity of the adsorbent. Furthermore, the results show that functionalized CNTs out-performed the non-functionalized CNTs during the desulphurization by about 10 %, indicating that functionalization of the CNTs did improve the desulfurization performance of the CNTs. Therefore, the percentage performances of the adsorbents were 70.48 % and 60.88 % for FCNTs and CNTs, respectively. Furthermore, the results on adsorption of DBT onto activated carbon (AC) show that large surface area of AC contributed to its performance removal of the DBT in model oil. The percentage performance of the adsorbents was 83.84 %.

The results presented in this current study using different adsorbents, have demonstrated that AC out-performed all other adsorbents used in this study, owing to its exceptional higher surface area, micro structure and porosity. Therefore, AC was chosen for desulfurization of South African diesel samples. The results showed that large surface area of AC contributed to its performance removal of the DBT in the diesel samples. The percentage performance of the adsorbents for desulfurization of diesel obtained after HDS (99 %) was higher than that of the diesel obtained before HDS (60.41 %) at the same initial concentration of 120 mg/L.

The adsorption mechanisms of the adsorbents were extensively described using Langmuir and Freundlich isotherms. The adsorption kinetic studies were described using pseudo first-order, and pseudo second-order kinetic models. The results of the adsorption mechanism show that both Langmuir and Freundlich isotherm models could describe well the mechanism of the adsorption process for all adsorbents used in this study. The pseudo second-order kinetics described the adsorption kinetics of the adsorption process for all the adsorbents as well.

As it has been demonstrated in this current study, AC was successfully immobilized in sodium alginate for adsorption of DBT in model diesel in a continuous packedbed column. This is a

promising method of entrapping adsorbent for maximum performance. AC has been widely reported in literature for column adsorption of sulfur compound from petroleum distillates. However, there are only few studies on the immobilization of activated carbon in sodium alginate for use in bed column for desulfurization of petroleum distillate. Results show that adsorption of DBT in a packed-bed column are dependent on superficial velocity of the sorbate solution through the adsorption column. The best result was obtained at the lowest superficial velocity of 0.031 m/min (0.5 mL /min) at 15 cm bed height and lowest initial DBT concentration of 100 mg/L. Furthermore, breakthrough time was found to increase with decreasing DBT initial concentration, decreasing flow rate and increasing bed height. The initial region of breakthrough curve was well described by the Adams–Bohart model at all experimental conditions studied while the transient stage or working stage of the breakthrough curve was described well by the Thomas kinetics model.

The results presented in this current study have shown that, *Pseudomonas aeruginosa* and *pseudomonas putida* were successfully grown in basal salt medium. The growing and resting cells of both bacteria were used to degrade the DBT molecule in the model diesel. Results show that *Pseudomonas aeruginosa* showed better BDS performance than *pseudomonas putida* in all aspect. The results in this study also showed that *pseudomonas aeruginosa* and *pseudomonas putida* are capable of desulfurizing DBT in model diesels into less harmful compound, 2- HBP. The final product 2-HBP detected shows the specific activity of DBT desulfurization is 4S-pathway. Results showed BDS performance of 67.53 % and 50.02 %, by resting cells of *Pseudomonas aeruginosa* and *Pseudomonas putida,* respectively for 500 ppm initial concentration. In order to study desulphurization of diesel obtained from an oil refinery, resting cells studies by *Pseudomonas aeruginosa* were carried out which showed a decrease of about 30 % and 70.54 % DBT removal from 5200 ppm in diesel obtained before HDS and 120 ppm in diesel obtained after HDS, respectively. *P. aeruginosa* and *P. putida* selectively converted sulfur atom in DBT compound to 2-HBP. The results obtained in this study showed that biodesulfurization would be a better process to compliment HDS process rather than the main technique for desulfurization of organo-sulfur compounds in diesel.

As it has been demonstrated in this current study, adsorption coupling biodesulfurization process (AD/BDS) was used to remove sulfur compound from two different South African diesel samples. The bed column experiment showed that superficial velocity in the ascending order 0.031 < 0.063 < 0.094 m/min, with flow rate in ascending order; 0.5 < 1.0 < 1.5 mL /min. Results also show that adsorption of DBT in a packed-bed column is dependent on superficial velocity of the sorbate solution through the adsorption column. The best result was obtained at the lowest superficial velocity of 0.031 m/min (0.5 mL /min) at 15 cm bed height and lowest initial DBT concentration of 120 mg/L. This means that, a longer breakthrough time is needed for higher performance of the bed column which will successively result in higher adsorption capacity.

The kinetic models studied in this present work show that, Thomas and Bohart-Adam's model describe well the kinetics of the adsorption process for model diesel as well as for the South African diesel samples. The Bohart-Adam model described the initial region of the breakthrough curve, while the Thomas model described the transient stage of the breakthrough curve. First order kinetic model described well the microbial degradation of DBT in the model diesel and South African diesel samples and Michaelis-Menten kinetic model described well the microbial growth. Therefore, it was used to describe its kinetics. The results obtained in this study showed that AD/BDS coupling process is efficient for desulfurization of South African petroleum distillate (e.g diesel)