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Performance Evaluation of Green Adsorbent (Neem Leaf Powder) for Desulfurization of Petroleum Distillate

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The release of sulfur-containing compounds during direct combustion of diesel fuel has caused environment issues which require urgent attention. Recently, stringent environmental regulations by the Environmental Protection Agency (EPA) to minimise the total sulfur-containing compounds released into the atmosphere have intensified the research in this area. In this present study, adsorption experiments in batch mode were conducted using an activated green adsorbent (Neem leaves powder) to reduce the amount of dibenzothiophene (DBT) in a synthetic oil. The synthetic oil was prepared by dissolving 0.1 g of dibenzothiophene (DBT) in 100 mL of hexane. Various analytical techniques were used such as; Scanning electron microscopy (SEM) to check the morphological structure of the adsorbent. Nitrogen adsorption and desorption experiments (Brunauer-Emmett-Teller, BET) at 77 K were used to check the surface area, pore size and pore volume of the adsorbent. N_2 physio-sorption at 77 K before and after adsorption showed adsorption of DBT molecules onto the surface of the adsorbent after adsorption experiment. The results showed about 65.78 % removal of DBT at temperature of 30^oC and adsorbent amount of 0.8 g. Therefore, neem leave powder could be an alternative cheap adsorbent to reduce the concentration of organo-sulfur compound in petroleum distillates. This may offer new perception into the development and application of green materials in sustainable, innovative and effective waste management and abatement of environmental pollution.
Keywords: Adsorbent, Adsorption, Diesel, Dibenzothiophene, Environment, Neem leaves powder

1. Introduction

Middle distillates can be referred to as a range of refined products located between heavier products such as fuel oil and lighter fractions, such as gasoline. These include kerosene, jet fuel, gas and diesel oils. During direct combustion of diesel, significant quantities of sulfur-containing compounds such as sulfur oxides (SO_2 and SO_3), sulfate particulate matter (PM) and sulfur-containing compounds (dibenzothiophene (DBT)) are released into the atmosphere. These result into acid rain and environmental pollution that is detrimental to human health (Monticello, 2000).Therefore, a stringent regulation has been passed to all refineries to minimize the emission of these sulfur compounds to a minimum level of ≤10 ppm. Currently, several existing techniques such as, biodesulfurization (BDS), extraction, biochemical processes (EBP), oxidation, adsorption (ADS) and hydrodesulfurization (HDS) have been used to reduce sulfur content in diesel fuel with different levels of success. HDS is the most frequently used technique for removal of sulfur compounds from petroleum distillates (Javadi and Klerk, 2012). HDS has succeeded in removing most of the simple sulfur containing compounds such as thiols, thiolates, sulfoxides, and sulfones. However, they are operated at elevated temperature and pressure. These high operating conditions are obligatory to desulfurize the most recalcitrant molecules with HDS method (Rashtchi et al., 2006). Even at elevated temperatures and pressures, many of the sulfur containing aromatic compounds and long chains remained, which result into reduction in the quality of fuel. The extreme conditions make HDS an expensive and energy intensive alternative for deep desulfurization (Folsom et al., 1999; Monticello, 1998; Sharaf, 2013). In addition, these result in reduction of

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catalyst life, higher consumption of hydrogen and higher cost of yield (Mei et al., 2003).Furthermore, HDS is not effective for removing heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) (Ismagilov et al., 2011). Equivalent of 70% sulfur-containing compounds in petroleum distillate exist as DBT. DBT, an organosulfur compound commonly present in common diesel is difficult to desulfurize using the traditional method (Hydrodesulfurization) which is presently in use (Monticcelo, 2000). Therefore, exploiting an efficient, readily available and cheaper technique to remove the sulfur containing compound from petroleum distillate in a relative green manner, so as to meet up with the strict guidelines regarding emission of sulfur oxides is still highly anticipated.

Adsorption method of desulphurization, among other techniques has been discovered to be a new efficient method of desulphurization in clean fuel research (Turku et al., 2009) due to its cost effectiveness, low energy consumption, as it can be performed at ambient temperature and pressure with possibility of adsorbent regeneration (Bamufleh, 2011). Different adsorbents such as metal−organic Framework Materials (MOFs), bentonite, palm kernel powder, activated carbon, rice husk, saw dust powder and carbon nanotubes, have been used to remove sulfur-containing compound from petroleum distillates. Currently, researchers have focused attention on the use of agricultural waste materials as potential adsorbents due to their ready availability and low cost for removal of various contaminants from wastewaters and fuels (Ahmaruzzaman and Gupta, 2011). Examples of such adsorbents include rice husk, saw dust, pomegranate leaves powder and Neem leaves powder have been used for removal of metal ions and organic pollutants from wastewater. The recycle of agricultural wastes and by-products for the purpose of removing sulfur-containing compounds from petroleum distillates is believed to reduce wastes in an eco-friendly way. Therefore, it's in agreement with concepts of sustainable, innovative and effective waste management (Nguyen et al., 2013).

Neem leaves powder (NLP) as adsorbent for treatment of DBT in petroleum distillates has not been widely reported. Therefore, from this point of view, neem leaves powder, which is an agro-based waste, could be a potential material for application in fuel desulfurization because of its ready availability and low-cost and will reduce environmental waste. Neem leaves are regarded as waste when the tree sheds the leaves. Neem leaves powder has been explored to proffer solution to various challenges related to environmental pollution, health wisely and in agriculture (Sharma et al., 2009). Reports have shown that neem leaves powder has a wider range of useful product compared to other plants (Pandhare and Dawande, 2013). Therefore, it can be used as an alternative low-cost adsorbent. Neem leaves powder has been used as an adsorbent in the removal of pollutants and colour from water and industrial effluents. Chromiun (VI) ion was adsorbed on Neem leaves powder in an experiment conducted by Sharma and Bhattacharyya (2004). In addition, Sharma and Bhattacharyya (2005) conducted an experiment using neem leaves powder as adsorbent to remove Cadmium (Cd) ion from aqueous medium. Jinturkar and Sadgir, (2017) used neem leaf powder as adsorbent for removal of iron from aqueous solution. Activated neem powder prepared using phosphoric acid was used for removal of phenol, 4-nitro phenol, and 4-chlorophenol from aqueous solution by Ahmaruzzaman and Gayatri (2011). Padhare et al. (2013) synthesized an activated neem leave adsorbent using ortho-H_3PO_4 as an activating agent and only BET analysis was done on it. In addition, neem leaves powder was used for desulfurization of real diesel by Daware et al. (2015). However, there is a need to study the adsorption desulfurization of DBT molecules which account for about 70 % of the sulfur organic compounds in diesel. Therefore, this study reports a novel and effective technique for removal of DBT from model diesel fuel, using a green-based adsorbent (neem leaves powder).This article, therefore studies the adsorption potential of neem leaves powder as a plant-based adsorbent to remove DBT from petroleum distillates

2. Experimental

2.1 Materials

Neem leaves powder was purchased from Organic choice (Ltd) South Africa, Dibenzothiophene (DBT), Acetonitrile (HPLC grade, 98 %) and Hexane 98% were purchased from Sigma Aldrich Pty (Ltd), South Africa. All chemicals were used without further purification.

2.2 Synthesis of adsorbent

The as-received NLP was activated by using H_2SO_4 as the activating agent. 20g of adsorbent was added to 10 mL of 0.5 M H_2SO_4. The mixture was stirred at 70 ^oC and dried at 110 ^oC in an oven for 2 h. The sample was then carbonized in a furnace at 500 ^oC for 3 h. It was washed severally with deionized water until a pH of 7 was reached in order to remove acid, and dried at 70 ^oC for 24 h. The dried activated NLP was ground and kept in a dry air-tight container until it was used in the adsorption experiment.

2.3 Characterization of adsorbents

The physio-chemical properties of the adsorbent were checked using scanning electron microscopy (SEM) for surface morphology. The surface morphology of neem leaves powder was observed using, CARL ZEISS sigma field electronic scanning electron microscope (FESEM) at different magnifications. The surface of the adsorbent was initially coated with Pd/Au before the commencement of the SEM analysis to avoid charge up. N2 physio-sorption experiments at 77 K to check the surface area, pore volume and pore size of the adsorbent. The textural property of the adsorbent powder was obtained using a Micromeritics Tristar 3000 static volumetric analysis unit through N2 physio-sorption experiments conducted at 77 K.

2.4 Product analysis

Model oil was prepared by dissolving 0.1 g of DBT in hexane (100 mL). After the adsorption experiment, High Performance Liquid Chromatography (HPLC, from Agilent) was used to analyze the desulfurized model oil. N-Hexane was used as mobile phase at wavelength of 280 nm, injection volume of 10 μl and 1.0 μl/ min flow rate, for 10 minutes.

2.5 Desulfurization experiments

The desulfurization experiments were carried out in batch mode using bio-sorbent neem leaves powder. Concentrations of the DBT, contact time, amount of adsorbent and operating temperature were varied during the experiment to determine the best operating conditions and parameters. Time dependent experiments were carried out for 180 min and samples were taken and analyzed at 10 min intervals. The solution was stirred and allowed to dissolve completely. Other dilutions were made from this solution to vary the concentration of DBT (250-1000 ppm). The values of adsorbent dosage were varied from 0.2- 1.0 g and were put into 20 ml of the model oil solution, each in an Erlenmeyer flask and agitated in a digitally monitored rotary shaker at three different temperatures (25-35 ^{o}C) at 130rpm for duration of 180 min. At varying intervals, aliquots of desulfurized model oil were taken for analysis. All experiments were carried out in triplicates to ensure accuracy and reduction of experimental errors.The mean value of the data obtained was used and the standard deviation was calculated. The percentage removal was calculated using Equation1. The final concentration of the DBT was obtained from calibration curve plotted from HPLC data. Absorbance data of known concentration was obtained and used to plot calibration curve in order to obtain mathematical relationship. Then, concentrations of the unknown samples were determined from the pre-determined calibration curve.

$$Percentage\ DBT\ removal\ (\%) = \frac{\text{Initial DBT concentration} - \text{Final DBT concentration}}{Initial\ DBT\ concentration} \times 100 \qquad (1)$$

3. Results and Discussion

3.1 Physio-chemical characterization of adsorbent

The physiochemical studies of neem leave adsorbent were studied in order to understand its texture. The textural properties contributed to the adsorption capacity of the adsorbent. N_2 Physio-sorption experiments for determination of textural properties such as surface area, pore volume and pore sizes of the adsorbents were carried out and measured before and after adsorption. The result in Table 1 illustrates that the surface area reduced from 73.13 m2/g to 53.60 m2/g, there was a reduction in the pore volume from 0.126 cm3/g to 0.074 cm3/g and pore size decreased from 34 nm to 13.158 nm after adsorption This could be an indication that some of the vacant adsorption sites of the adsorbents present initially before adsorption process had been filled up with DBT molecule after adsorption had taken place.

Table 1: N_2 Physio-sorption parameters of NLP before and after adsorption experiment

NLP	Surface area (m^2/g)	Pore volumes (cm^3/g)	Pore sizes (nm)
Before adsorption	73.21	0.0126	34.00
After adsorption	53.60	0.0736	13.16

SEM images of neem leaves powder are shown in Figures 1(a) before adsorption,(b) after adsorption, and (c) at 5th cycle re-usability.In Figure 1a, It can be seen apparently that neem leaves powder has an irregular surface structure and the pore stuctures are not well-defined. This structural state favors the adsorption of DBTs (Ghaneian et al., 2015).Figure1b showed the attachment of DBT on the surface of the used adsorbent.

However, Figure 1c showed that some of the adsorption sites of the adsorbent have been blocked after being re-used for four times. This slightly affected the adsorption capacity, since adsorption capacity of an adsorbent is dependent on its surface properties. This observation is confirmed in Table 1 where there were reductions in the values of surface area, pore volume and pore size after adsorption experiment.

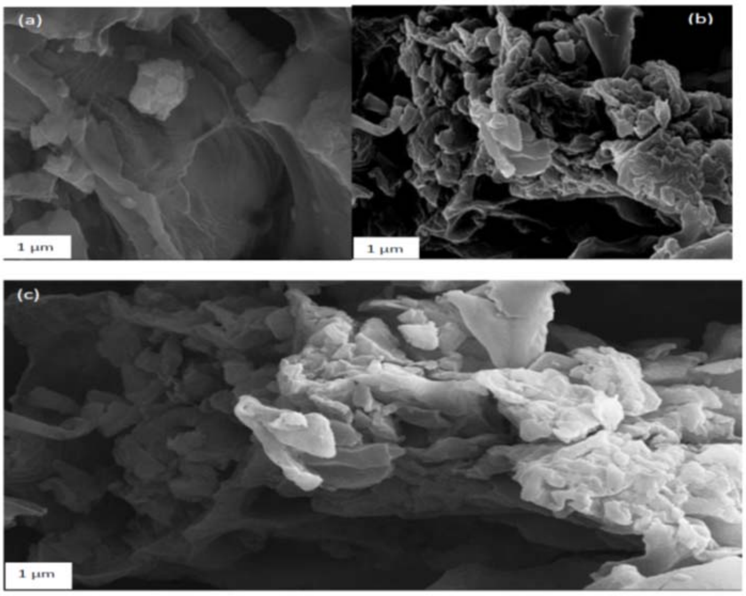

Figure 1: SEM images of Neem powder (a) before adsorption and (b) after adsorption (c) at fifth re-usability cycle

3.5 Effect of desulfurization parameters

Figure 2 depicts the influence of amount of adsorbent on the adsorption capability of NLP. The results showed that, as the amount of adsorbent increases, the percentage of sulfur adsorbed on the surface of the adsorbents also increased. This trend could be attributed to the availability and accessibility of more adsorption sites and more surface area for sulfur compound attachment (Srivastav and Srivastava, 2009; Ahmad et al., 2015; Daware et al., 2015) on which adsorption process is dependent. Therefore, desulfurization yield is increased. It was observed that, as the amount of adsorbent increased from 0.8 g to 1.0 g, there seemed to be no more significant increase in the adsorption capacity of NLP (Marı´n-Rosas et al., 2010). This could result from increase in viscosity and inhibition of DBT molecules diffusion to the surface of NLP (Gonga et al., 2009; Yasemin and Ayse, 2011). In addition, it could be due to unavailability of vacant sites on the surface of the adsorbent. This is favourable in possible application of neem leaves powder for removal of sulfur-containing compounds in petroleum distillates at a minimum amount of adsorbent.

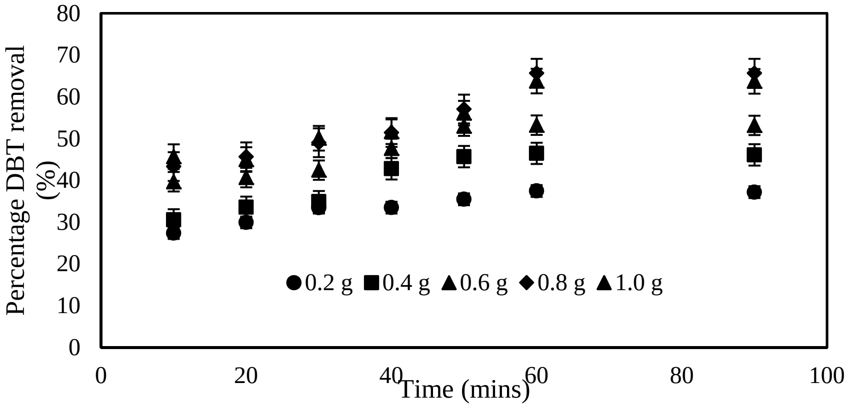

Figure 2: Effect of adsorbent amount on desulfurization of model oil at equilibrium temperature of 30 ^oC. at varying adsorbent amount

3.7 Effect of DBT concentration on the feed stream

The concentration of DBT in the feed was varied in the model oil since diesel contains DBT in varying concentration. The initial concentrations ranged from 250 -1000 mg/L as shown in Figure 8. Other operating conditions were kept constant; adsorbent amount (0.8 g), temperature (30^oC), volume of model oil (20 mL), and contact time (60 min). From the result obtained in Figure 3, it could be deduced that DBT adsorption per unit mass of adsorbent increased as the initial concentration increased. This could be attributed to the concentration gradient developed the surface of the adsorbent and the DBT solution which is as a result of increased mass transfer driving force. The same result was observed by Ishaq et al. (2017).

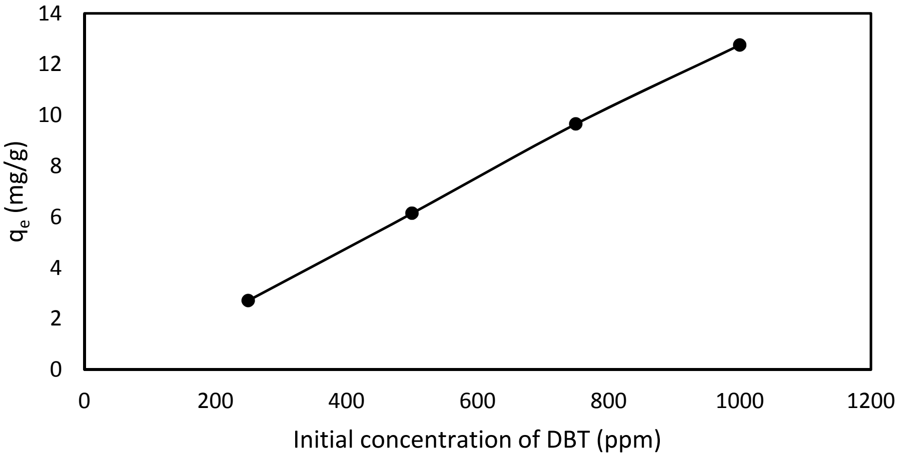

Figure 3: Effect of initial concentration on adsorption of DBT on neem leaf adsorbent. Experimental conditions: Contact time: 60 min, stirring speed: 130 rpm, adsorbent amount: 0.8 g, and temperature: 30^{o}C.

4. Conclusion

The conclusions derived from this study are as follows:

- It can be concluded that the structural surface of the adsorbent contributed to the adsorption capacity of the adsorbent
- N_2 adsorption desorption experiments and SEM results confirmed the adsorption of DBT molecules onto the surface and pores of the adsorbent.
- The highest desulfurizing capacity of the adsorbent was 65.78 % at maximum conditions of 60 minutes, 0.8 g adsorbent amount and temperature of 30 ^{o}C.
- Neem leaves powder can be of great value in commercial application since it can be reused up to four times without losing its potential strength of removing DBT from petroleum distillate.
- A higher percentage DBT removal is obtained at reduced amount of neem leaves powder adsorbent. This will promote its commercial application.
- Therefore, this shows that cheap, readily available and less energy intensive plant-based adsorbent (Neem leaves powder) could be effective for removal of sulfur containing compound from petroleum distillates to meet up with the strict policies regarding emission of sulfur oxides.

In a nutshell, a proof of concept has been established from the use of this novel agro-based adsorbent for the removal of sulfur-containing compound (DBT) in a model diesel. This could help in the development and application of green materials as a novel and an effective management of waste and reduction of pollution in the environment.

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