Synthesis, Characterization and Performance Evaluation of Pure Silica MCM-41 for Effective Removal of Dibenzothiophene from Petroleum Distillate

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Abstract

The presence of sulfur-containing compound (e.g. Dibenzothiophene, DBT) in petroleum distillates such as diesel is of great concern due to the environmental problems it poses on the environment. In this study, synthesis and performance evaluation of MCM-41 adsorbent for enhanced removal of DBT from petroleum distillates in batch adsorption mode is reported. MCM-41, employed in this study for adsorptive desulphurization, was successfully synthesized with Cetyltrimethylammonium bromide (C₁₉H₄₂BrN) and fumed silica (SiO₂). The gel was stirred for 30 min at room temperature and allowed to age at varied durations (24 h, 48 h & 72 h) before hydrothermal synthesis and then calcined at 550 °C. Different analytical techniques were used to characterize the synthesized adsorbents, such as: Fourier transform infrared (FTIR) to check the surface nature, N₂ physi-sorption at 77 K to examine the textural property; Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) to check the surface morphology/elemental composition; and X-ray diffraction (XRD) to check the crystallinity of the adsorbent. The adsorptive desulphurization experiments were carried out using a model diesel prepared by dissolving 0.1 g of dibenzothiophene in 100 mL of hexane. The desulfurized model diesel was analyzed using Gas Chromatography/Mass Spectrometer (GC/MS). The adsorption performance of each adsorbent was evaluated in a batch mode. The results showed that, aging time has significant impact on the crystallinity and textural properties of MCM-41. The results show that crystallinity increased with decreasing aging period with smaller surface area as compared to adsorbent whose gel was aged for more hours. Furthermore, the textural properties seem to improve as the aging time increased. MCM-41, whose gel was aged for 72 h showed the highest adsorption capacity of 36.2 mg/g with highest DBT removal of 96.5 %. The information and results presented in this study could therefore provide a platform for further studies in this field.

Keywords: Adsorption; Dibenzothiophene; Diesel; MCM-41; Petroleum distillates; Pure silica.

1. Introduction

The global energy demand has increased exponentially recently and it is anticipated to increase by 13.4% between 2013 and 2040. Among the energy sources available globally, petroleum remains the major resource of energy with numerous wide-ranging applications [1].
In South Africa for example, fossil fuel energy consumption was reported in 2014 at 86.91% of which 80% is being used in transportation according to the World Bank collection [2]. Fuel is a major source of energy for running different equipment and machinery. The most widely used types of fuel are petrol and diesel. Diesel is obtained as a distillate in the fractional distillation of crude oil in the petroleum refinery. Diesel is widely used as fuel in diesel engines. Owing to this, the diesel fuel market is estimated to grow steadily in the near future. 2017 was reported the strongest year for global oil growth demand, with diesel continuing to play a substantial role. In 2017, diesel demand accounted for 430 Kb/d [3]. By 2025, about 35 % growth of the share of diesel fuel in the transportation sector is anticipated, because of the advanced economic development and trade in the developing nations, resulting into significant growth in the transportation sector [3]. However, the existence of compounds of sulfur in crude oil distillates like diesel is unwanted, due to their expensive process and environmental issues [4].

Sulfur occurs in various forms in crude oil such as; sulfur, hydrogen sulfide (H₂S), mercaptans, sulfides, disulfide, thiophenes, dibenzothiophene (DBT) [2]. However, these forms of sulphur are unwanted in petroleum products because of their possible environmental challenges such as pollution, resistance to octane booting, corrosion of the equipment, pollution and catalyst poisoning during catalytic hydro treatment [4, 5]. Health concerns like cancer, cardiovascular disease, respiratory diseases and asthmatic symptoms are as a result of emission of sulphur compounds during combustion of diesel. Their emission into the atmosphere also result into smog, acid rains, deforestation, air pollution and global warming. Furthermore, sulphur compounds cause deactivation of catalysts used in processing of diesel oil, cause corrosion in pipeline, pumps, and refining devices. In addition, catalytic converters that are used in automotive engines are poisoned. Sulfur compounds also cause early failure of combustion engines [6].

Gaseous SOx at high concentrations damage the foliage thereby causing harm to trees and plants and hampering their growth. Emission of SO₂ and other sulfur oxides during direct combustion of diesel contribute to acid rain and has adverse effect on the ecosystems. Acid rain is as a result of transportation of the emitted sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) by wind and air currents in the atmosphere. Sulfuric and nitric acids are formed when the SO₂ and NOₓ react with moisture, oxygen and other chemicals and then falls as rain [2]. The negative outcome of acid rain on the environmental is most evident on the aquatic habitats. The lives of fishes and other wildlife are endangered when acid rain washes the aluminium in soil clay into the streams and lakes [7].

Over 80 % of the overall sulfur content present in transportation fuel are thiophene sulphides, out of which benzothiophene (BT) and dibenzothiophene (DBT) alone account for about 70 % [2]. Thus far, hydrodesulfurization (HDS) is the only known conventional technique for the treating organosulfur in the refinery. It has been reported to be highly effective for treating aliphatic and acyclic sulfur-containing compounds like disulfides, sulfides and thiols in transportation fuel [2, 3, 5]. However, less efficient for removing thiophene sulfides like dibenzothiophene and its derivatives. Furthermore, HDS is generally operated under high temperature and pressure thereby making the process expensive. Based on these extreme conditions, several other non-HDS techniques have been explored, such as, adsorption [8], extraction [9], biodesulfurization [10], electrochemical technology [11] and oxidation [12]. Among these techniques, adsorptive desulfurization (AD) is the best known promising techniques for desulfurization of fuel, which is usually carried out at low temperature and
Numerous adsorbents have been used by many researchers. However, adsorbent with high surface area and improved adsorption capacity, with high thermal stability is urgently required. Efforts have been made to improve heterogeneous catalysts so as to obtain highly active selective material needed. Zeolites have been discovered to be effective alternative materials as catalysts for processes in the chemical and petrochemical industries [13]. Zeolites are reported to possess pores with molecular dimensions, high adsorption capacity, high specific surface area and high hydrothermal and thermal stability [14]. Nevertheless, zeolites show limitations to the diffusion of bulky molecules due to their tiny micropores. This leads to increase in reaction time resulting in coke formation which causes the deactivation of zeolite by blocking the channels [15]. Extensive investigations have been carried out to synthesize zeolites containing mesopores with the same size as MCM-41 so as to overcome the diffusion limitations. MCM-41 has well-ordered mesopores however show lower acidity and lower hydrothermal and thermal stability. Therefore, several approaches which involves the use of templates (surfactants) for generating mesoporosity that produces solids with the intrinsic microporosity with narrow pore size distribution had been investigated [16]. This approach resulted in a well-arranged hexagonal mesophases of MCM-41-type which offer hydrothermal stability and acidity to the mesoporous structure. Effect of synthesis parameters like temperature, seed aging time, gel composition and crystallization temperature on the properties of mesoporous materials had been evaluated. However, few studies have shown that aging period of MCM-41 seeds formation is an essential factor affecting the properties of the synthesized material.

In view of these, synthesis, physico-chemical characterization, of pure silica MCM-41 at different aging times are presented in this study. In addition, the performance evaluation of the synthesized adsorbent for effective desulfurization of petroleum distillate (e.g. DBT from diesel) is reported.

2. Materials and methods

2.1. Materials

Cetyl-trimethylammonium bromide ($\text{C}_{19}\text{H}_{42}\text{BrN}$) 98% and Silver nitrate 99.5% from Radchem Inc., South Africa, Fumed silica 99.8%, Sodium hydroxide 98%, Hydrochloric acid 37%, hexane CP (98 %), and Dibenzothiophene (DBT) were obtained from Sigma Aldrich (Pty) Ltd, South Africa. Cerium chloride ($\text{CeCl}_3\cdot\text{H}_2\text{O}$) 98.5% from Merck.

2.2. Synthesis of pure MCM-41

The pure silica MCM-41 was prepared with fumed silica and Cetyl-trimethylammonium bromide (CTMAB) ($\text{C}_{19}\text{H}_{42}\text{BrN}$) solutions. 0.26g of $\text{C}_{19}\text{H}_{42}\text{BrN}$ was added to 150 mL of deionized water and agitated on a magnetic stirrer at 300 rpm for 30 minutes, at room temperature. To the solution, 1.58 g of fumed silica and 1 M sodium hydroxide was added under magnetic stir at 300 rpm at 60 C and stirred for 10 min at room temperature. Then the pH was adjusted to 11 with Hydrochloric acid. The gel was stirred for 30 min at room temperature. The gels were transferred to three PE bottles and allowed to age at room temperature without agitation at different durations labelled (24 h, 48 h, 72 h). After ageing, the aged solution was transferred into a Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at autogenous pressure at 140 C for 2 days. The solid products were
washed using distilled water using Hettich Rotofix 32 A centrifuge at 30 rpm X 100 in 15 minutes until the filtrate tested negative for Br– using silver nitrate. The solids products were then dried at room temperature and finally calcined at 550 °C for 5 h.

2.3. Characterization of pure silica MCM-41 adsorbent

The morphologies of the adsorbents were checked using Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX). In order to prevent charge up, the samples were pre-coated with 60 % Palladium and 40 % Gold (Pd/Au) before SEM analysis. Jeol JEM 1200 EXII equipment was used to perform transmission electron microscopy (TEM) analysis. One drop of the suspension of samples dispersed in ethanol was positioned onto the surface of the carbon-coated copper grids (150 mesh).

Nitrogen physi-sorption experiments at 77 K were performed on the adsorbents to check the textural properties of the adsorbents. The surface area, cumulative pore volume and pore diameters of the adsorbents were determined using Micrometrics tristar 3000 static volumetric analyzer unit. This information was obtained from liquid nitrogen at 77 k equilibrium isotherms. Brunauer–Emmett–Teller (BET) model was used to calculate the specific surface areas. The estimation of pore volumes was performed at a relative pressure of \((P/P_0)\) range of 0.05–0.30, with full surface saturation with nitrogen. Barrett–Joyner–Halenda (BJH) model evaluated the pore size distributions from desorption branches of nitrogen isotherms. The total pore volume \((V_p)\) was determined by Nitrogen adsorbed at a relative pressure near 1 \((P/P_0 = 0.995)\). The determination of average pore diameter \((D_p)\) was done from the \(N_2\) desorption isotherms using BJH method and equation (1) was used in estimating the pore wall-thickness \((W_t)\):

\[
W_t = a_0 + D_p
\] (1)

Fourier transform Infra-red analyzer, Bruker Tensor 27 at a spectra range of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) was used to check the surface functionalities and the functional groups present on the surfaces of the adsorbent samples. X-ray diffraction spectroscopy (XRD) was used to check the crystallinity of the adsorbents. The characterization was performed on a Bruker D2 X-ray diffractometer to identify the phases of the adsorbent \((\lambda = 0.15418 \text{ nm})\). The measurement range was at 20 to 100 \((2\theta)\) at upper angles. The phases were confirmed using EVA software with PLU2018-pdfs-4-2018RD database. Bragg's equation in Equation 2 was used to estimate the d-spacing value \((d_{100})\) from the position of the first X-ray diffraction line and Equation (3) was used in calculating the unit cell parameter \((a_0)\) for a hexagonal lattice [17]

\[
2d_{100}\sin\theta = n\lambda
\] (2)

Where \(d\) represent the interplanar spacing of the crystal, integer \(n\) is the “order “of reflection, \(\Theta\) is incidence angle and \(\lambda\) is the wavelength of the incident x-rays.
2.4. Performance evaluation of MCM-41 adsorbent in batch mode

The performance evaluation of the MCM-41 synthesized adsorbent was carried out by performing the desulfurization experiments in a batch mode. Three different synthesized adsorbents with varied durations (24 h, 48 h & 72 h) were evaluated for enhanced DBT removal from model diesel. The desulfurization experiment was performed at different operating conditions; DBT concentrations (250 mg/L), reaction time (30 minutes), mass of adsorbent (0.8 g) and temperature (25 °C) to determine the best adsorbent with highest adsorption capacity. At 10 mins intervals, samples of treated oil were taken and analysed. To prepare the model oil, 0.1 g of DBT was dissolved in 100 mL of hexane. After DBT had completely dissolved in hexane, the solutions were further diluted to make DBT concentration of 250 mg/L. About 0.8 g of adsorbent was added to 20 mL of the model oil and allowed to stir on a magnetic stirrer at 25 °C at 130rpm for duration of 30 min. In order to ensure accuracy of result and reduce experimental errors, all experimental procedures were performed in triplicates. To obtain a mathematical relationship, calibration curve was plotted from the absorbance data of known concentration obtained from HPLC to calculate the final unknown DBT concentration. The percentage removal was calculated using Equation (4):

\[ \text{Percentage removal} (\%) = \frac{\text{Initial DBT concentration} - \text{Final DBT concentration}}{\text{Initial DBT concentration}} \times 100 \] (4)

The adsorption capacity for each run of the experiments was determined using Equation (5):

\[ q_e = \frac{V}{m} \left( C_0 - C_e \right) \] (5)

Where \( C_0 \) and \( C_e \) are the initial and final DBT concentration in mg/L, in the model oil respectively, \( m \) is adsorbent amount in g and \( V \) is the volume of the model oil (L).

3. Results and discussion

3.1. Surface morphological of pure silica MCM-41

Figures 1A, 1B and 1C show the surface morphologies and porosities of pure MCM-41 silica that were aged at different times. The samples exhibit two regular sphere shaped particles having rough surface morphologies. It could be seen that increasing concentration of CTMAB causes rate of growth of mesoporous silicon layers becomes wider, resulting in spherical-like particles. At varying amount of surfactant and solvents, different textures and morphologies are observed [18]. Bhattacharyya et al. [18], stated that in the absence of alcohol as a co-solvent in synthesis of MCM-41, SEM images show only spherical structures. This could be as a result of packing parameter of the surfactant, \( g \), which is dependent on the total volume of the surfactant chain plus any co-solvent molecules between the chain [19]. Bhattacharyya et al. [18], reported that, surfactant the phase configuration in the synthesis of
mesoporous materials depends on the packing parameter, $g$. Curved surface such as MCM-41 ($1/3 < g < 1/2$) is stabilized by small values of $g$. Results of Zana and Talmon [19] showed that ammonium surfactants like CTMAB, can form only spherical micelles. When the concentration of CTMAB is increased, larger number of micelles are formed and more hexagonal units grow into smaller final size. Lastly, usually high adsorption capacity of adsorbent is associated with its rough morphology and high porosity [18]. The results showed that samples that were aged for 48 h and 72 h have bigger regular spherical particles and number of particles increases with size and number. This is an indication that, the longer the aging period, the more time is made available for the grains to aggregate and form larger particles. Similar observations of MCM-41 has been reported in the work of Sajjadi et al. [16].

![Figure 1: SEM images of pure MCM-41; (A) 24 h (B) 48 h and (C) 72 h.](image)

### 3.2. EDX analysis of the synthesized adsorbents

The Energy Dispersive X-Ray Spectroscopy (EDXS) analyses of the prepared adsorbents at different aging times were performed so as to determine their elemental compositions before
desulphurization. Figures 2 A to 2 C show the EDXS spectra and elemental compositions of pure MCM-41(24 h), MCM-41(48 h) and MCM-41(72 h). It can be observed that percentage weight of oxygen reduced with increasing aging period of the pure silica MCM-41 from 55.92 % (24 h) to 40.77 % (72 h). However, the percentage weight of silicon increased with increasing aging period from 69.01 % (24 h) to 45.28 % (72 h). The EDX micro-analytical data for pure MCM-41 shows that Si-O contents were in homogeneous and near stoichiometric values and confirmed the structure of the synthesized MCM-41 [16].

3.3. TEM images for pure Silica MCM-41

Figures 3 A and 3 B show the micrographs of pure MCM-41 taken by transmission electron
microscope (TEM) at different magnification of 100 nm and 200 nm. Even though MCM-41 is amorphous silica in nature, it has an ordered structure having uniform mesopores arranged into a hexagonal, honeycomb-like lattice as displayed by the micrographs in Figure 3 A. In Figure 3 A, there is a uniform mesopore inside separated from each other by thin walls of amorphous silica. The mesopore are curved and are not running through the silica matrix, therefore the hexagonal order is maintained, as seen in Figure 3 A. From the micrographs it is apparent that MCM-41 because of the presence of the mesopores has very large void fraction and low density. This gives MCM-41 a large specific surface area. This property makes MCM-41 an effective material to be used in adsorption processes. Vadia et al. [20] observed that long tubes are gradually formed when the concentration of the surfactant in water is increased. As the concentration is increased further, aggregates of the rod-like micelles is changed into a hexagonal liquid crystalline structure, which resembles MCM-41 structure. Xiu at al. [21] reported that as the concentration of the template is increased, polymerization of the silicate species is increased and therefore the average head group area (A) of the surfactant assembly increases because of the decrease in the charge density of bulky silicate layers and eventually resulted into hexagonal mesophases precipitation. The most honeycomb and hexagonal shapes of MCM-41 are reported by Grecco et al. [13], Sajjadi et al. [16], Vadia et al. [20] and Mardali and Zahra [22].

![Micrographs of pure MCM-41](image)

Figure 3: TEM micrographs of pure MCM-41

3.4 Nitrogen adsorption isotherms

Nitrogen N₂, physi-sorption experiment was performed to check the textural properties (such as pore size, surface area, pore geometry and pore volume) of the adsorbent. The extent to which estimated surface area is related to micro, meso-, and or macropores is revealed using this technique. Figure 4 depicts the typical nitrogen adsorption-desorption isotherms of samples prepared at 24 h, 36 h and 72 h aging time.

According to IUPAC classification, type IV isotherms are obtained for these materials [15]. From Figure 4, there are five distinct regions that can be observed from the graphs. Nitrogen physi-sorption at these reduced pressures is generally attributed to condensation of nitrogen inside the micropores of a material. Conversely, MCM-41 is totally a mesoporous material
and in the absence of micropores [23]. At region I, monolayer nitrogen adsorption process occurred both on the internal and external surface of the mesopores of MCM-41 [20]. At region II, upon monolayer adsorption, there is progression of multilayer of nitrogen at increasing relative pressures of nitrogen. Furthermore, both the external surface area and the mesopores contributed to the physisorption process [23].

Figure 4: Nitrogen adsorption-desorption isotherm of pure MCM-41 (24, 48, 72 h)

A sudden steep increase at a relative nitrogen pressure of about 0.35 at region III is the amount of nitrogen adsorbed. The increase in steep is due to capillary condensation of nitrogen inside the mesopores. This is when the liquid nitrogen fills the mesopores of MCM-41 all of a sudden, owing to the filling of the mesopores which occurs at a moderately small range of relative pressures, $P/P_0$ between 0.34 – 0.4. During this process, the associated pores must be approximately the same in size [24]. Region IV is usually related to the multilayer adsorption of nitrogen on the outer surface of the MCM-41. It can be seen that the slope is very shallow at this region indicating small external surface area of MCM-41 [23]. Lastly, nitrogen uptake by the sample increases again when the relative pressures is near value of 1. These feature can be attributed to condensation of nitrogen within the interstitial voids between the particles of MCM-41 [23]. Xiu et al. [21], Teymouri et al. [25] and Broyer et al. [26], results showed that MCM-41 exhibits reversible type IV isotherm without hysteresis, which is the case in the present study. Desorption isotherm happen together with the adsorption process and there is no hysteresis loop observed. Teymouri et al. [25] reported that this observation is as a result of the adsorption and desorption processes that are reversible in this region, indicating that most pores within the sample are open pores. Their accessibility to the nitrogen molecules has made them to be directly connected to the surface of the calcined sample. For all samples that had aged at different times in this present work, type IV isotherms without hysteresis were obtained (Figure 4).

For comparison, Figure 4 shows that the formation of the adsorption- desorption isotherms is affected by increase in aging period. The results show that the uptake at 0.35 becomes more
pronounced with increasing aging time. This indicate the steady increase in pores formation [25]. Furthermore, the increase in aging time led to more homogeneous pore distribution.

Table 1 shows the pore properties, pore diameter ($D_p$), specific area ($S_{BET}$), and pore volume ($V_p$) of pure MCM-41 samples at different aging times. The specific surface area was calculated from the linear section of the BET plot. The mean pore diameter was determined from the $N_2$ absorption data, using the BJH (Barrett-Joyner-Halenda) method. The pore diameter was subtracted from the lattice parameters $a_0$, so as to calculate the wall thickness. The pore diameters confirm the mesoporous nature of the synthesized materials with pore size distribution between 2 and 6 nm which are in the range typically observed for MCM-41 samples [26]. For comparison, large-pore volume samples are seen in the samples that were allowed to age at 24 and 48 h (0.8 cm$^3$/g) but 0.5 cm$^3$/g for the sample that aged at 72 h. However, the huge values of pore volumes have relatively thin pore walls, 2.3 and 2.4 nm for 24 h and 46 h samples respectively. The results obtained from this study show that, as the aging time increased, there was increase in surface area from 410 to 673 m$^2$/g. Sayari et al. [27] suggested that, the thin pore wall is an indication that the prepared MCM-41 has low stability. All the observations agree with the reports of Vadia et al. [20] and Suyanta et al. [15].

Table 1: Pore structural parameters of the corresponding samples

| Sample (hour) | Pore diameter (nm) | Wall Thickness (nm) | Surface Area (m$^2$/g) | Pore Volume (cm$^3$/g) |
|--------------|--------------------|---------------------|------------------------|------------------------|
| 24           | 6.2                | 2.3                 | 410                    | 0.8                    |
| 48           | 4.7                | 2.4                 | 520                    | 0.8                    |
| 72           | 5.3                | 2.8                 | 673                    | 0.5                    |

3.5. Crystallinity of pure silica MCM-41

Table 2 illustrates reflections assigned to (100) plane in the highly ordered hexagonal arrangement of pores with d100 spacing of 4.04 nm, 3.29 nm, and 3.86 nm for 24 h, 48 h and 72 h, respectively. Figure 5 depicts the wide-angle X-ray powder diffraction (XRD) patterns of the synthesized pure MCM-41. A broad diffusion peak or an amorphous peak centred with the equivalent Bragg angle at $2\theta = 23$ and 32 was noted, signifying that the main substance synthesized silica MCM-41 is amorphous silica framework [27, 28]

The aging time sensitively influenced the intensity of the d100 peak of the samples. From Figure 5 the intensity becomes higher as the aging increases. At 24 h aging time, the intensity is higher compared to 48 h and 72 h intensities. The relative intensities of the d100 were therefore used to measure the relative crystallinity of the samples as presented quantitatively in Table 2. It can be seen that, the gel aged for 24 h has the highest crystallinity of 95 %, followed by 48 h with 85 % and 72 h is the lowest with 75 %. Increasing the aging time causes the adverse effect on the intensity of d100 peaks. It can be assumed that the siloxane (Si-O-Si) groups formed in the previously process can stimulate the formation of hydrogen bonding with water molecules. Eventually, those siloxane groups were hydrolysed and part of the well-organized hexagonal structure broken according to the reaction in Equation (6):
\[=\text{Si-O-Si}= + \text{H-O-H} \rightarrow =\text{Si-OH} + \text{HO-Si}=\] (6)

After the depolymerisation, the hydrolysed silicate seems to turn to interact with remain rode micelle, this lead to the formation of the hexagonal liquid crystalline phase. The formation can be caused by the hydrothermal treatment [15]. Table 2 shows the interplanar d and the distances between pore centres \(a_0 = \frac{2}{3^{1/2}}d\). The value of \(a_0\) are spread over the range of 3.79 to 4.66. It can be assumed that the difference in aging time can affect \(a_0\). The trends in this work is in accordance with the work of Sayari et al. [27], Zakaria et al. [28], Suyanta et al. [15] and Reza et al. [29].

![Figure 4.5: XRD pattern of MCM-41 (24 hr., 48 h & 72 h)](image)

| Samples (hr) | d(100) (nm) | \(a_0\) (nm) | Crystallinity % |
|-------------|-------------|---------------|----------------|
| 24          | 4.04        | 4.66          | 95             |
| 48          | 3.29        | 3.79          | 85             |
| 72          | 3.86        | 4.45          | 75             |
3.6. FTIR spectra of pure MCM-41

Figure 6 describes the FTIR spectra of calcined pure MCM-41 in the wave number region of 400-4000 cm\(^{-1}\) after calcination. All the spectra show the sharp bands around 1077 cm\(^{-1}\) and 1376 cm\(^{-1}\) wave number which is characteristic for vibration of symmetric and asymmetric stretching of O-Si-O bridges respectively. These bridges are the part of silicates polymer formed in the hydrothermal treatment. The hydroxyl broad absorption band is in the region between 3000 and 3700 cm\(^{-1}\). The hydroxyl absorption bands were observed at 3338 to 3678 cm\(^{-1}\). This band is associated with stretching of Si-O-H group in the framework perturbed by physically adsorbed water molecules. The weak band at 798 cm\(^{-1}\) to 800 cm\(^{-1}\) of wave number assigned the stretching of Si-O- group. The bands were also observed in the work of Broyer et al. [26], Suyanta et al. [15] and Grecco et al. [13].

![FTIR spectrum of pure MCM-41 (24 h, 48 h, & 72 h)](image-url)

3.7. Performance evaluation of pure MCM-41

Figure 7 depicts the DBT percentage removal by adsorbents aged at varied durations (24 h, 48 h & 72 h). Table 3 shows the adsorption capacity, \(q_e\). Percentage removal and adsorption capacity of the adsorbent were calculated using, Eq. 1 and Eq.2, respectively. The results from Figure 7 showed rapid intake of DBT adsorption for the first 10 min., after which the adsorption rate steadily decreased. The higher rate of adsorption at the initial stage may be as a result of more accessible vacant sites on the surface of the adsorbent. As time proceeds, the concentration of DBT molecules in the vacant sites, resulting in a reduction in the adsorption rate afterward. Figure 7 also shows that, the adsorbent that had its gel aged for 72 h (MCM-41\(_{72\,h}\)) has the highest percentage removal of 96.5 %. In Table 3, the \(q_e\) values of the adsorbent are at the average of 11.4 mg/g, 10.3 mg/g and 11.8 mg/g for 24, 48 and 72 h, respectively.
It could be concluded from the results that the adsorbent whose gel was aged for 72 h has the best adsorption capacity. This can be attributed to its best textural properties and crystallinity compared to others as was determined by N₂ adsorption experiment and XRD characterization. MCM-41(72 h) has the highest specific surface area, largest pore volume, lowest crystallinity and the SEM images showed that it has rough surface. All these properties could be responsible for its highest adsorptive capacity [30]. The results show that, aging time on MCM-41 could improve the adsorption capacity. The observations were also seen in the works of Suyanta et al. [15]. Thus, making MCM-41 a promising adsorbent for adsorption of DBT in batch mode which could also be utilized in continuous mode.

![Figure 7: Comparative percentage removal for MCM-41 (24 h, 48 h and & 72 h)](image)

Table 3: Adsorption capacity of pure MCM-41 at different aging times. Volume of model oil; 20 mL, concentration of DBT; 250 mg/L and mass of adsorbent; 0.8 g

| MCM-41 aging time (hours) | Time (min) | qₑ (mg/g) |
|---------------------------|------------|-----------|
| 24                        | 10         | 5.8       |
|                           | 20         | 11.6      |
|                           | 30         | 16.9      |
| 48                        | 10         | 5.6       |
|                           | 20         | 10.8      |
|                           | 30         | 14.6      |
| 72                        | 10         | 6.1       |
|                           | 20         | 11.7      |
3.8. **Comparison of results with literature**

Table 4 shows that the results obtained in this study are comparable with literature. Sadare et al. [8] desulfurized the DBT in a model oil using pomegranate leaf powder. It could be seen that the result obtained from this study showed 96.5 % removal of DBT from the model oil while 70.8 % DBT was achieved by Sadare et al. [8]. Although, the result from this current study out-performed the work of Sadare et al. [8], however a higher initial concentration of DBT (1000 mg/L) was used compared to 250 mg/L that was used in this current study, which could have contributed to its performance. In addition, longer contact time was allowed compared to 10 minutes that was allowed in this study. Ahmed and Ahmaruzzaman [31] used chemically impregnated coconut coir waste to treat petroleum distillate. Their results showed 67 % DBT removal at initial DBT concentration of 250 mg/L, at 180 min. contact time. However, there was a higher percentage removal of 96.5 % recorded from the current study at lower contact time of 10 minutes and initial concentration of 250 mg/L. This result could be attributed to the treatment the MCM-41 (72 h) adsorbent underwent during aging.

| Adsorbent | Model oil | Amount of ads. (g) | Time (min) | C<sub>a</sub> (mg/L) | C<sub>f</sub> (mg/L) | % SR | Ref. |
|-----------|-----------|--------------------|------------|----------------------|---------------------|-------|-----|
| PLP | DBT | 1.0 | 60 | 1000 | 294.5 | 70.8 | [8] |
| NLP | DBT | 0.8 | 60 | 1000 | 342.2 | 65.8 | [10] |
| AC | DBT | 2.0 | 60 | 1000 | 199.0 | 80.1 | [10] |
| CICCW | DBT | 2.0 | 180 | 250 | 82.5 | 67.0 | [31] |
| MCM-41 | DBT | 0.8 | 10 | 250 | 8.75 | 96.5 | This study |

C<sub>a</sub> is the initial concentration of DBT; C<sub>f</sub> is the final concentration of DBT; Ads. is adsorbent and % SR is the percentage of sulphur (DBT) removal; PLP is pomegranate leaf powder; NLP is Neem leaf powder; AC is activated carbon and CICCW is chemically impregnated coconut coir waste.

4. **Conclusions**

In conclusion, different samples of pure silica MCM-41 at different aging time have been successfully synthesized and it has been established that MCM-41 is an alternative adsorbent for removal of sulphur containing compound from petroleum distillate like diesel. As far as it can be established, no investigation has been conducted on the application of MCM-41 (aged at different times) to effectively remove DBT from petroleum distillates. From the results obtained in this study, aging time has shown to have great impact on the crystallinity and the textural properties of MCM-41. The results show that the adsorbent which had aged for few hours has high crystallinity but smaller surface area compared to adsorbent which had aged for more hours. In other words, the textural properties seem to improve as the aging time is increased. The results show that synthesized pure silica MCM-41 adsorbents have good adsorption capacity of 36.2 mg/g for desulfurizing the model diesel. However, the best adsorption capacity is demonstrated by the adsorbent that had been allowed to age for the
longest time. The results further show high percentage removal (R %) of 96.5 % by adsorbent with the highest aging time (72 h). Based on the outcome of the study, it has been established that MCM-41 is a promising and effective adsorbent for desulfurizing petroleum distillate (diesel). The information obtained in this study could therefore provide a platform for further studies in this field.

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