

Research Article

Synthesis of Multiwalled Carbon Nanotubes-Titania Nanomaterial for Desulfurization of Model Fuel

Tawfik A. Saleh, Mohammad N. Siddiqui, and Abdulrahman A. Al-Arfaj

*Department of Chemistry and Center of Research Excellence in Nanotechnology (CENT),
King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Correspondence should be addressed to Mohammad N. Siddiqui; mnahid@kfupm.edu.sa

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This work reported on the development of novel nanomaterials of multiwalled carbon nanotubes doped with titania (CNT/TiO₂) for the adsorptive desulfurization of model fuel oils. Various analytical techniques such as field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR) were used for the characterization of the nanomaterials. The initial results indicated the effectiveness of the prepared CNT/TiO₂ nanomaterials in removing sulfur compounds from model fuel oil. The adsorption of DBT, BT, and thiophene from model fuel onto the derived sorbents was performed using batch mode system. These CNT/TiO₂ nanomaterials initially afforded approximately 45% removal of DBT, 55% BT, and more than 65% thiophene compounds from model fuels. The CNT/TiO₂ nanomaterials provided an excellent activity towards interaction with organosulfur compounds. More experiments are underway to optimize the parameters for the adsorptive desulfurization processes. We believe that these nanomaterials as adsorbents will find useful applications in petroleum industry because of their operational simplicity, high efficiency, and high capacity.

1. Introduction

The amount of sulfur contents in fuels often provides indication to the emission of SO_x gases, which are responsible for the formation of sulfates and acid. Moreover, several corrosion problems in pipelines, pumping, and refining equipment may also occur as a result of sulfur-contents emission. Sulfur emissions also cause deleterious effects on human health. In order to reduce the sulfur contents in diesel fuels, the environmental regulation agencies have introduced an allowable limit of 10 ppm with the ultimate goal of further reducing SO_x gases emissions. As a result of the aforementioned environmental regulations, there have been several reports successfully reducing the organic sulfur contents in diesel fuels to less than 10 ppm. For instance, of the various desulfurization techniques, hydrodesulfurization (HDS), oxidative desulfurization, biodesulfurization, and adsorptive desulfurization are being investigated for their ability to produce clean fuels. One of the current industrial methods for removal of sulfur from fuels is HDS,

for reducing of organic-sulfur in gasoline, diesel, and other intermediate distillates where various catalysts are used. HDS process removes many organosulfur compounds and their derivatives from transportation fuels; however, this method has certain limitations and is less effective at the removal of sterically hindered dibenzothiophene derivatives such as 4,6-dimethyldibenzothiophene, which are most prominent in diesel fuels. Some suggestions such as the use of more active catalysts, longer residence times, and higher temperatures and pressures have been reported for improving the effectiveness of HDS for producing low sulfur product [1]. Therefore, to meet the demands of producing ultraclean fuels with lower than 15 ppm of organosulfur compounds via HDS will increase both monetary investment and operational costs. Consequently, it is imperative that advanced technologies be developed for desulfurization at ambient temperature and pressure. Currently, the most common HDS alternative method used to achieve ultraclean fuels is adsorptive desulfurization (AD) where π -complexation is free of steric hindrance for adsorption [2–4].

One-dimensional nanoscale structure of nanotubes with covalent bonding together imparts unusual properties: high tensile strength, high resilience, and good thermal and mechanical stability. Porous carbon also has properties such as uniform and regular pore size and structure, chemically inert, pore network interconnected with tailorable surface properties [5]. Such properties make CNT a good adsorbent and catalyst support. Thus carbon nanotubes could be used as support in nanocomposite materials. Activated carbon has been reported [6] to have good adsorption ability toward methyl substituents of organic sulfur compounds such as 4,6-DMDBT that is a refractory compound for desulfurization of diesel.

Adsorption of organic sulfur compounds in diesel fuel to composite adsorbents has been reported in recent years. A comparison between activated carbon, alumina, and MWNT and their corresponding composite catalysts with cobalt and molybdenum oxide and sulfide shows that dibenzothiophene (DBT) adsorbs to two kinds of sites, one is the acidic sites and another is on the transition metals with vacant orbits which can accept electrons. In case of sulfide state adsorbent, newly produced active sites on the edges of active phases provide higher adsorption compared with oxide states [7]. Fe_2O_3 -NPs supported on CNT was employed as a catalyst for the desulfurization of H_2S in a classical fixed-bed configuration [8]. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{MWNT}$ supported catalyst has been reported as effective catalyst for the oxidative removal of DBT, with high desulfurization efficiency [9]. However, the adsorption capability should depend on the quality of the interfacial contact between CNTs and TiO_2 . Literature screening indicates that the carbon materials like carbon nanotubes, graphenes, and their composites are promising candidates for improving the activity of nanoparticles by preventing their agglomeration and thus maintaining their high surface area [10–15].

Some approaches have been reported for the synthesis and preparation of TiO_2/CNT composite. This includes direct in situ growth, in situ CVD synthesis route, high-intensity ultrasonic radiation method, assembling presynthesized metal oxide nanoparticles as building blocks on CNTs, spontaneous formation of metal oxide nanoparticles on CNTs, hydrothermal crystallization, sol-gel followed by spark plasma sintering process, surfactant wrapping sol-gel method, and chemical precipitation [16–19].

We report here a procedure for desulfurization of model fuel oil by adsorption on $\text{MWCNTs}/\text{TiO}_2$ nanomaterials. Thus, the nanomaterials were synthesized and characterized. The desulfurization activity was evaluated by model fuel of thiophene, benzothiophene, and dibenzothiophene.

2. Experimental

2.1. Materials and Chemicals. Multiwalled carbon nanotubes (CNTs) were with specifications of purity, >95%; outer diameter, 30–50 nm; inner diameter, 5–10 nm; 30–50 nm; length, 10–20 μm ; average specific surface area, 60 m^2/g ; electrical conductivity: >100 S/cm; bulk density: 0.28 g/cm^3 ; true density: $\sim 2.1 \text{ g}/\text{cm}^3$. Thiophene, benzothiophene, and

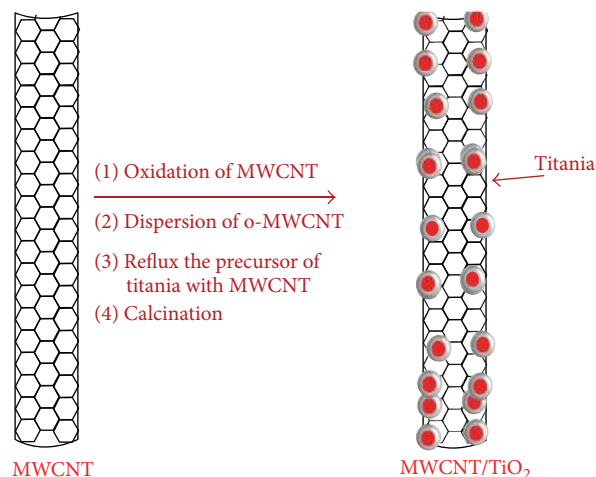


FIGURE 1: Schematic diagram of preparation of $\text{MWCNT}/\text{TiO}_2$ nanomaterials.

dibenzothiophene were obtained from Fisher Scientific Company. The solvents employed in all the studies were of high purity. Other reagents were of analytical purity, obtained from Sigma Aldrich and used as received.

2.2. Preparation of CNT/TiO_2 Nanomaterials. CNTs were purified and oxidized before use. After the purification process, nanotubes were treated with a mixture of HNO_3 and H_2SO_4 as reported earlier [20, 21]. In brief, nanotubes were refluxed in a mixture of H_2SO_4 - HNO_3 (3 : 1) for 8 h at 120°C . The mixture was diluted, filtered, and washed with deionized water to remove the excess acid from this solution. After that, it was dried overnight at 120°C in an oven, and then it was milled and crushed to powder.

CNT/TiO_2 nanomaterials were prepared by the following steps. Nanotubes were dispersed by sonication for 4 h at room temperature. At the same time the precursor of titania, titanium tetraisopropoxide solution, was hydrolyzed and stirred until it progressively became more viscous. The former, then, was drop-wise added with continuous stirring [22]. Then, it was refluxed for 6 h. Then, the mixture was washed and filtered. Then, it was dried overnight. The final step is the calcination for 3 h at 350°C . Then, the composite was characterized using various instruments. Figure 1 depicts a schematic diagram of CNT/TiO_2 nanomaterials preparation.

2.3. Characterization. The characterization of the CNT/TiO_2 nanomaterials is important to evaluate the interaction between titania nanoparticles and the nanotubes. Therefore, the characterization was performed by means of field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared absorption spectroscopy (FTIR). The specific surface area of the CNT/TiO_2 nanomaterials was determined by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.05 to 0.4.

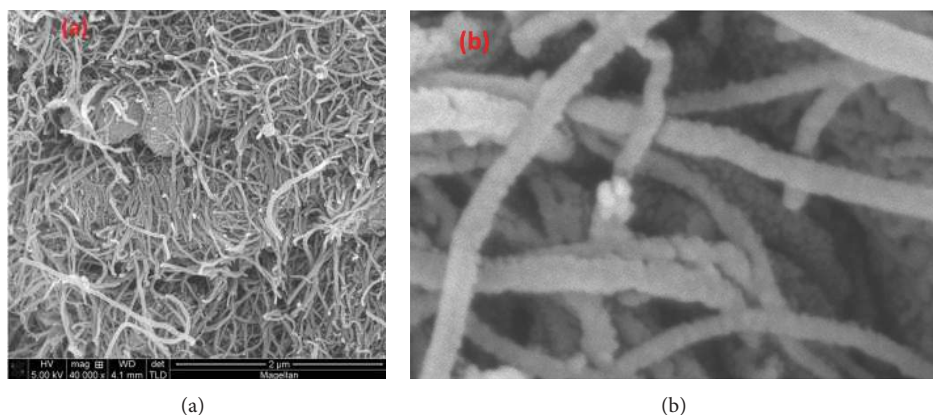


FIGURE 2: High resolution field emission scanning electron microscopy (FESEM) image (a) and enlarged SEM image (b) of the MWCNT/TiO₂ nanomaterials.

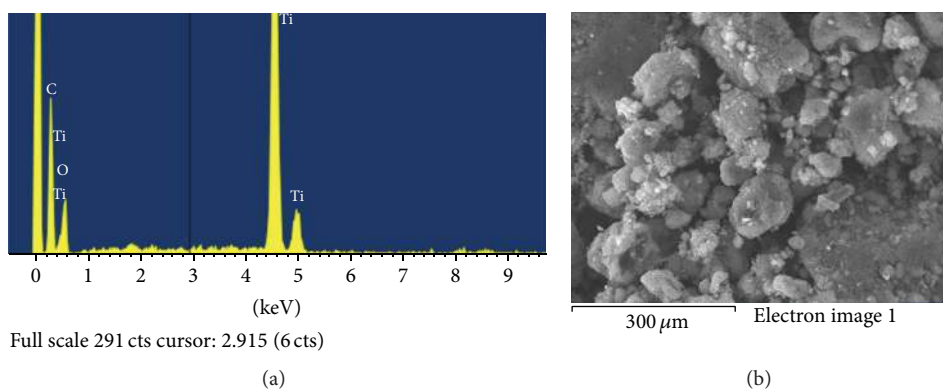


FIGURE 3: EDX spectrum and SEM image of the MWCNT/TiO₂ nanomaterials.

3. Results and Discussion

3.1. Characterization. The surface morphology of the prepared nanotubes/titania nanomaterials was characterized by high resolution field emission scanning electron microscope (SEM). The SEM image is depicted in Figure 2(a) and enlarged part of SEM image is depicted in Figure 2(b). The surface morphology of TiO₂ nanoparticles is ball like round shape or spherical shape decorated on the nanotubes. Based on these findings, one can induce that the nanocomposite has been successfully obtained and titania nanoparticles were deposited on the surface of the nanotubes [23, 24].

The EDX analysis was also carried out for the synthesized CNT/TiO₂ nanomaterials. The EDX spectrum is depicted in Figure 3. The spectrum confirms the presence of the carbon, oxygen, and titanium elements, which formed the CNT/TiO₂ nanomaterials. Table 1 presents the elemental analysis of nanomaterial with weight and atomic percent. EDX analysis showed the presence of oxygen, nitrogen, carbon, and relatively high titanium content on the nanomaterials. Table 1 presents the elemental analysis of nanomaterial with weight and atomic percent.

The nitrogen adsorption-desorption measurement at -160°C indicates that the prepared nanocomposites have a specific surface area of $158\text{ m}^2\cdot\text{g}^{-1}$. These high surface and

TABLE 1: EDX elemental analysis of the MWCNT/TiO₂ nanomaterials.

Element	Weight %	Atomic %
C K	31.80	50.85
O K	27.29	32.76
Ti K	40.90	16.40
Totals	100.00	

rough surface morphologies are expected to enhance the adsorption for such applications. The molecular structure of nanomaterials was characterized by FT-IR as shown in Figure 4(a). The FTIR spectra of nanomaterials show that bands at 1580 and 1650 cm^{-1} are ascribed to the stretching vibrations of C=C and C=O on the nanotubes, respectively. The peaks at 1400 and 1100 cm^{-1} are ascribed with the C-O stretching. The FTIR spectrum of nanomaterials shows the characteristic peak of Ti-O bond at around $600\text{--}700\text{ cm}^{-1}$, and the characteristic peaks of carbonyl, hydroxyl, and unsaturated carbon bonds in the composite. [25, 26]. The structure of nanocomposite was characterized by XRD as shown in Figure 4(b). The XRD pattern of the CNT/TiO₂ nanomaterials confirms the presence of titania of anatase

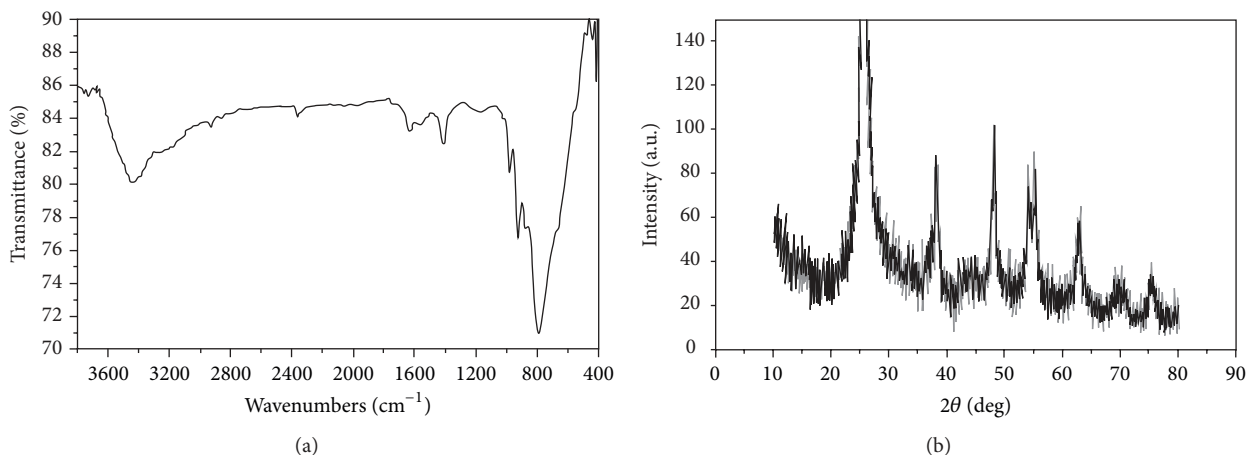


FIGURE 4: FTIR spectrum (a) and XRD (b) of the MWCNT/TiO₂ nanomaterials.

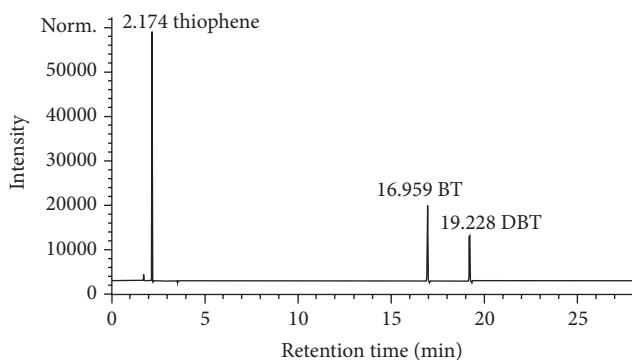


FIGURE 5: Gas chromatogram of desulfurized oil by MWCNT/TiO₂ nanomaterials; thiophene, benzothiophene (BT), and dibenzothiophene (DBT).

phase. The peak at 25.8° correspond to the (002) reflection of CNTs and the anatase TiO₂ peak (101) at the reflection plane of $2\theta = 25.3^\circ$. The peaks in the XRD pattern at 37.80 (004), 48.18 (200), and 54.09 (105) clearly represent the anatase TiO₂ phase. From the XRD pattern, it can be understood that the anatase constitutes the major crystal form in CNT/TiO₂ composite [27].

3.2. Desulfurization Activity. The work was conducted to evaluate the desulfurization activity of the CNT/TiO₂ nanomaterials. The desulfurization activity was evaluated by model fuel of thiophene, benzothiophene, and dibenzothiophene. Figure 5 depicts a shot screen of gas chromatogram of desulfurized oil by CNT/TiO₂ nanomaterials. The initial results revealed the effectiveness of the prepared nanomaterials in removing sulfur compounds from model fuel oil. From a comparison between the activity of CNT, titania mechanical mixture of titania and CNTs (MM), and the prepared CNT/TiO₂ nanomaterials, it was found that the CNT/TiO₂ nanomaterials have better desulfurization activity than others. Figure 6 depicts the results in percent. As shown

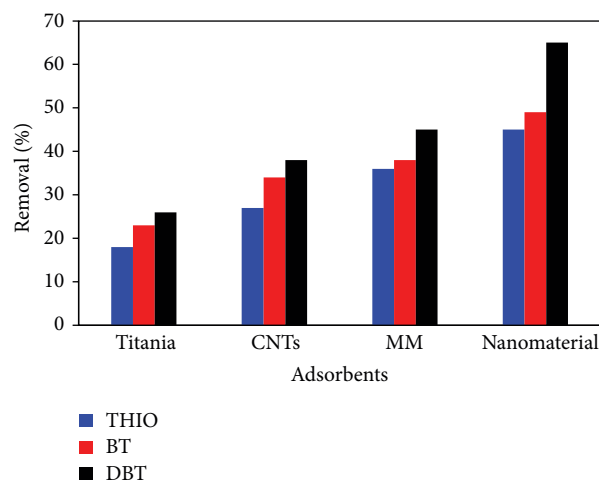


FIGURE 6: A comparison between the desulfurization activity of CNT, titania, mechanical mixture of titania and CNTs (MM), and the prepared CNT/TiO₂ nanomaterials; thiophene (THIO), benzothiophene (BT), and dibenzothiophene (DBT); conditions: reaction time is 60 min; agitation speed is 150 rpm; temperature is 23°C .

in the figure, the nanomaterials have better desulfurization activity; this can be explained by the fact that CNT as a support plays an important role in determining the nature and number of active sites and, consequently, in the activity of the nanoparticles. CNTs play also a role in inhibiting the in situ agglomeration/aggregation during the operation and thus help maintain the catalytic activity.

The efficiency of sulfur removal is significantly influenced by the amount of adsorbent used. The effect of the mass of adsorbents versus percentages of sulfur adsorbed was investigated for the CNT/TiO₂ nanomaterials. The amounts of thiophene, BT, and DBT adsorbed onto the adsorbents are depicted in Figure 7. A trend of increment in adsorption capacity with increment in adsorbent dose was observed from 0.1 to 0.75 g. The results indicate that the amount of

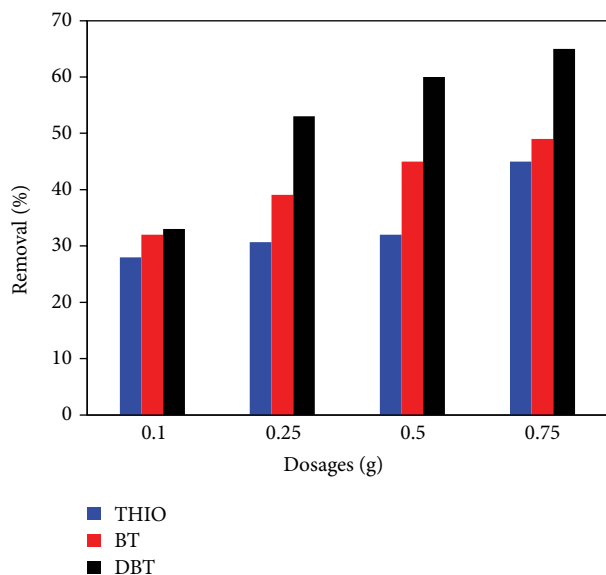


FIGURE 7: Effect of CNT/TiO₂ nanomaterials adsorbent dosage on the adsorption of thiophene (THIO), benzothiophene (BT) and dibenzothiophene (DBT).

sulfur compounds adsorbed by the adsorbent increased with increasing the amount of the adsorbent. The initial increase in adsorption capacity with increase in adsorbent dosage was expected because the increase in the number of adsorbent particles results in more surface area and more adsorption sites [28] available for sulfur compounds attachment.

DBT exhibits higher percentage of removal for each dosage and on all adsorbents due to the ability of DBT to form π - π dispersive interactions between the aromatic ring in DBT and the nanotubes with nanoparticles. This also can explain that the molecules with three aromatic rings (DBT) showed a significantly higher adsorptive affinity than two-ring aromatics (BT) and higher than one ring (thiophene) [29].

4. Conclusions

In summary, we have evaluated and compared the desulfurization activity of CNT, titania, mechanical mixture of titania and CNTs (MM), and the prepared CNT/TiO₂ nanomaterials for the adsorption of thiophene (THIO), benzothiophene (BT), and dibenzothiophene (DBT). It has been observed that prepared CNT/TiO₂ nanomaterials have better desulfurization activity than other tested materials. We believe the CNT/TiO₂ nanomaterials, as adsorbent, will find useful applications in petroleum industry because of their operational simplicity, high efficiency, and high capacity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

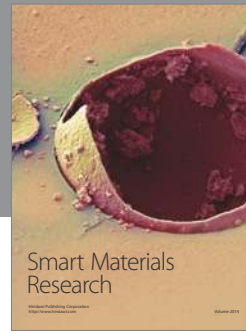
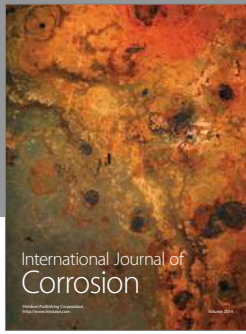
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