RESEARCH PAPER

# Comparison of the Efficiency of Titanium and Molybdenum Nanometal Oxides as Adsorbents for Sulfur Compounds in Crude Oil

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ABSTRACT

The sulfur content in crude oil and its derivatives negatively affects all aspects of life, especially economic, environmental and industrial. It is vital to create methods and materials that are both affordable and environmentally friendly in order to remove sulfur from crude oil. for this purpose titanium oxide ($TiO_2$) and molybdenum trioxide ($MoO_3$) nanoparticles were prepared by hydrothermal method at different temperatures and characterized by several techniques including using scanning electron microscopy (SEM), x-ray diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FT-IR), zeta potential, and dynamic light scattering (DLS) to find out some physical and chemical properties of the prepared nano compounds, The results showed that ($MoO_3$) was more efficient than ($TiO_2$) in reducing the sulfur content of crude oil. This work presents a successful example of the preparation of $TiO_2$ and $MoO_3$ NPs based hydrothermal method and the successful application of these NPs as active components, for the potential sulfur compound adsorbents, supporting environmental treatment.

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## INTRODUCTION

The economic, agricultural and industrial development and the steady increase in the automobile industry lead the world to the increasing demand for crude oil, which prompted scientists to devise easy and cheap ways to remove sulfur from crude oil and its derivatives and raise its quality by reducing the sulfur content [1-4]. From the lowest percentage of 0.05% to the highest percentage of 14% by weight depending on the source of crude oil, and the sulfur content in transportation fuels such as gasoline and kerosene must be less than 10 ppm according to environmental regulations [5,6]. Crude oil contains both organic and inorganic sulfur compounds (active sulfur), both sulfur and hydrogen sulfide, and light mercaptans that can interact directly with the metal. As for the organic sulfur compounds (inactive sulfur) thiophene, thiol, dibenzo thiophene, benzo thiophene and many complex molecules that cannot interact directly with the metal, which in turn form sulfur oxides when the fuel is oxidized and thus cause health and environmental problems [7,8]. Crude oil treatment techniques can remove impurities and pollutants, especially sulfur pollutants, which can be treated by conventional methods, using a combination of physical, chemical and biological

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methods [9,10]. Many refineries use a variety of procedures to reduce the sulfur content of crude oil. Adsorption desulfurization (ADS) and oxidative desulfurization (ODS) are the most important desulfurization methods for many reasons, including moderate operating conditions, good desulfurization effect and high selectivity of thiophene compounds [11,12].

In the adsorption technique, the sulfur compounds present in the hydrocarbons are adsorbed on the solid surface made of an adsorbent material, where the adsorption efficiency depends on the selectivity of the adsorbent material, the most important examples of adsorbent surfaces are zeolite, activated carbon, silica, alumina and titanium dioxide, which drew the attention of researchers for its instinctive properties Which played an important role in the removal of heavy metals [13].

It was also known as an environmentally friendly catalyst with little activity in ultraviolet radiation, which led to its use in many fields, including the field of environmental treatment [14,15]. Titanium dioxide exists in three forms; brookite, rutile, anatase. While the method of oxidation desulfurization is a new method for removing sulfur under moderate conditions (temperature and pressure) and has a low cost compared to the hydrogenation desulfurization method(HDS), molybdenum trioxide was recently selected as a promising material for oxidation desulfurization, molybdenum has many oxidation states (+2 - +6) Which makes it attractive to researchers, as molybdenum trioxide is one of the most important oxides because of its excellent physical and chemical properties, and most importantly its distinct multi-layered structure and interesting optical and electrochemical properties [16]. There three types of $MoO_3$: “Thermodynamically stable ortho-rhombic a-$MoO_3$, the metastable monoclinic b-$MoO_3$ and hexagonal h-$MoO_3$” Molybdenum oxides have many uses in electronics, energy storage units, vital systems, sensors, superconductors, biomaterials, and lubricants [17]. Adsorption and oxidation desulfurization technology can be combined to produce an ultra-low sulfur fuel. The removal efficiency was observed less when using nanoscale titanium oxide 3.5% while using nano molybdenum oxide 14.9%

## MATERIALS AND METHODS

Sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) from Merck, Germany Titanium isopropoxide (97%, Sigma-Aldrich), ethanol (99.9%), hydrochloric acid (37%), Ascorbic acid, Sodium decyl sulfate (SDS), Hydrogen peroxide (50%, Panreac applab., Spain), Formic acid (95%, Sigma-Aldrich).

*Preparation Procedure*

Prepare $TiO_2$ nano particles was as carried out according to previous published study by ( N.S. ANWAR, A. KASSIM, H.N. LIM, S.A. ZAKARYA, N.M. HUANG) [1] With some modifications by Titanium


Fig. 1. Used oil analyzer (SLFA-6100).

isopropoxide (5 ml ) was added dropwise in to a mixture of (2.5 ml) ethanol and (3.5 ml) dilution HCl while stirring and a clear solution was formed , After that was added 10 ml SDS ( 1.0 wt %) under stirring at room temperature for 15 mints , the mixture was then transferred in to a Teflon-lined autoclave and put it is in the oven at 120 C for 24 hr. , then it is cooled at room temperature and product is separated by centrifuge , washed with water and ethanol , then dried at 60 C for 24 hr. and then stored overnight in a desiccator.

Prepare α- $MoO_3$ nano -belts articles was as carried out according to previous published study by researchers (Amani Jabbar Obaid and Luma Majeed Ahmed) [2] With some modifications by using 1 mmol Sodium Molybdate dihydrate with 7ml HCl dilution(added in the form drops) while stirring for 15 mints then added 10 ml of ascorbic acid solution with mixing by a magnetic stirrer , the mixture was transferred to steel Teflon tube autoclave and hydrothermal reaction was carried out at 180 C for 6 hr. , the result is also separated and washed with water and ethanol , and dried in an oven at 60 C for 6 hr. and then stored overnight in a desiccator.

*Desulfurization Procedure*

Two solutions are prepared by mixing 25 ml of prosses oil taken from the (Bazerkan field in Maysan) with (2 ml) hydrogen peroxide, (2 ml) formic acid with (2 ml) distilled water and equal amounts of (0.4 g) of binary Titanium oxide for the first solution and molybdenum trioxide for the second solution. These solutions are symbolized by the symbols S1 and S2, respectively. The solutions, S1, S2, are placed in a water bath at (500) revolutions per minute and (50 $^{o}$C) for an hour and a half. The solutions are cooled at

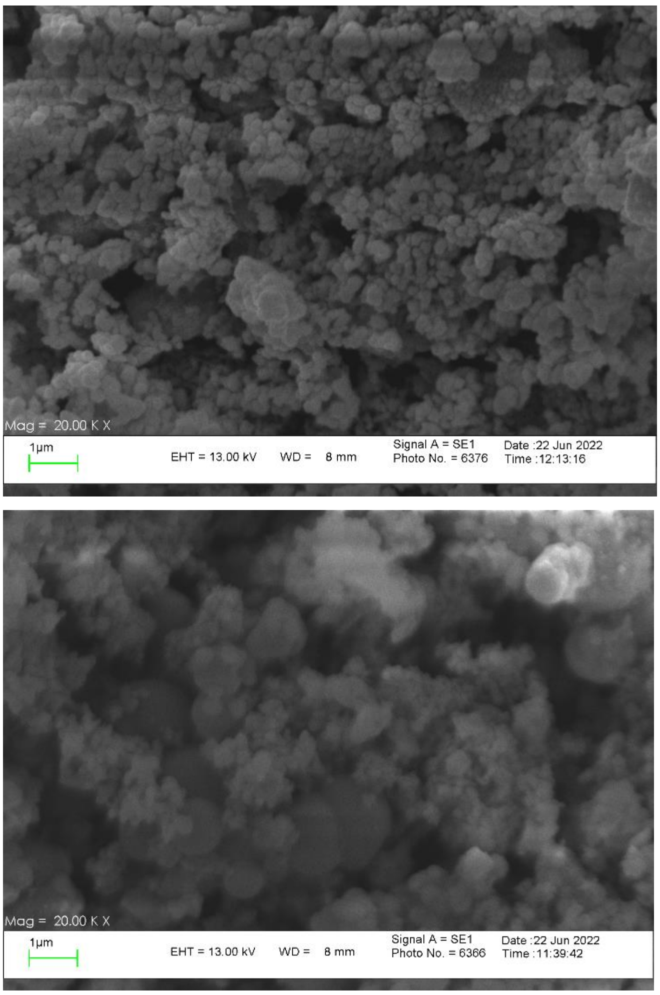


Fig. 2. SEM image of A) produced $TiO_2$-NPs B) produced $MoO_3$-NPs

room temperature, then the nanomaterials are separated from them using a centrifuge from the oil solution. The sulfur content of the two models S1, S2 is measured with the original sulfur content measured in the original model S0 (the treated oil) by an X-ray fluorescence Sulfur in oil analyzer. SLFA-6100 in Misan Oil training institute is shown in the Fig. 1.

## RESULTS AND DISCUSSION

### *Characterization of nano Oxide*

Nanocomposite materials' size, aggregation state, and morphology are all important considerations in this field. Consequently, to assess the surface morphology of nanocomposites, scanning electron microscopy was employed, as shown in SEM images. According to the SEM images, the produced $TiO_2$ nanoparticles morphology was shown in Fig 2.A which appeared as spherical NPs with size diameter about 34 nm. While $MoO_3$ NPs was shown in Fig 2. B. which indicated that The nanoparticles were spherical form with 41 nm in size.

It is possible to examine the phase composition and crystal size of the generated NPs using X-ray diffraction analyses.

The standard XRD peaks of Anatase $TiO_2$ are in good agreement with the peaks in the $TiO_2$ XRD pattern (Fig. 3) corresponding to (JCPDS Card No. 040477). The $MoO_3$ diffraction peaks that can be precisely indexed to pure $MoO_3$ are shown in Fig. 4. (JCPDS data file no. 05-0508).

### *(FT-IR) Fourier-Transform Infrared Spectroscopy*

The FTIR spectra of $TiO_2$ and $MoO_3$ NPs were shown in Figs. 5, and 6. Broadband with a center at 3419 $cm^{-1}$ is thought to be responsible for the stretching vibration of the -OH on the oxide surfaces under varied conditions. The broad bands in the $TiO_2$ spectrum that are centered between 500 and 600 $cm^{-1}$ are responsible for the bending vibration (Ti-O-Ti) bonds.

### *Analysis of the sulfur content of crude oil*

The measurement of sulfur content in the treated and untreated oil samples was performed

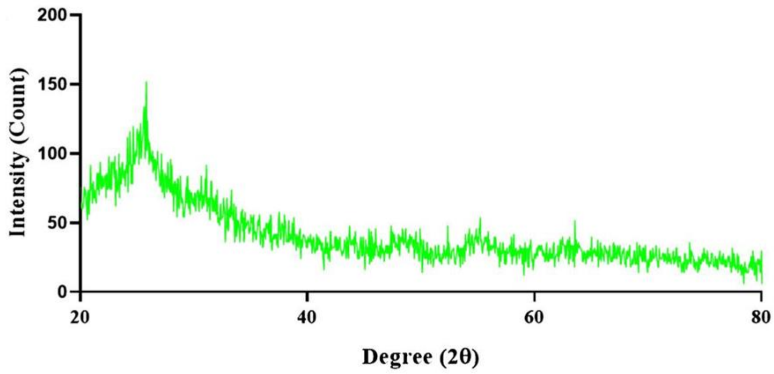


Fig. 3. XRD of $TiO_2$ nano particles

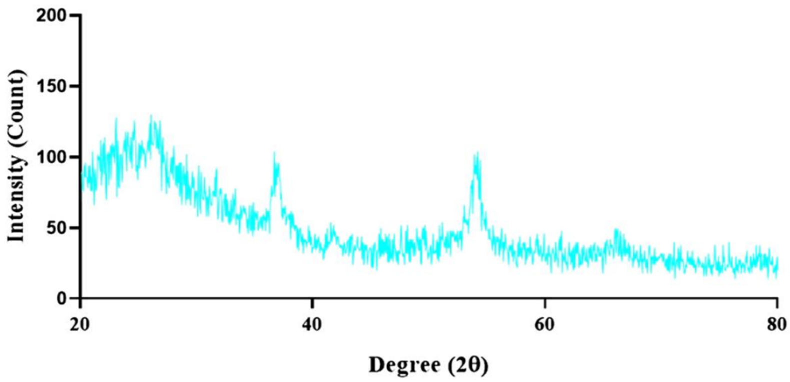


Fig. 4. XRD of $MoO_3$ nano particles


Fig. 5. FT-IR of $TiO_2$ nano particles

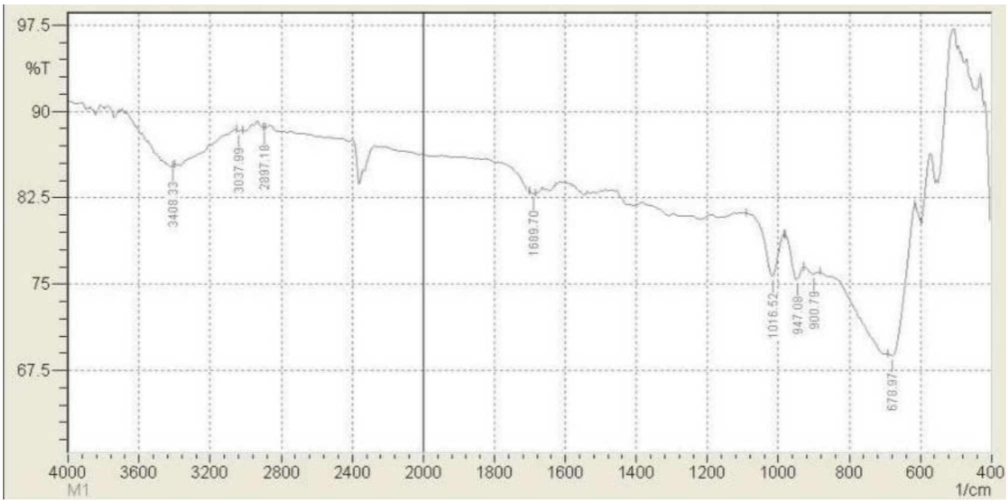


Fig. 6. FT-IR of $MoO_3$ nano particles

by X-ray analysis. The desulfurization percentage is obtained as the ratio of the sulfur that is reduced (or removed) to that present in the crude oil as in the following equation

$$\mathrm{DE} = ( S_o - S_m / S_o) \times 100\ \%$$

Where:

DE: desulfurization efficiency

$So$: the sulfur content of the original oil sample

$S_m$: the sulfur content in the oil sample after treatment.

The used nanomaterials showed the highest removal efficiency when using nano molybdenum oxide 14.9%. This may be attributed to the removal by oxidation as a synergistic function with the adsorption that is characteristic of this compound. However, the removal efficiency was observed less when using nanoscale titanium oxide 3.5% less, which depends only on removal by adsorption.

Nanomaterials have peculiar characteristics in contrast to their bulk counterparts. Their high surface-to-volume ratio confers unique physiochemical characteristics, such as a variety of functions and increased reactivity or selectivity [18-25]. Numerous products, processes, and applications that might surely support environmental and other biological applications can make use of nanotechnology's distinctive properties [26,27].

## CONCLUSION

The increasing demand for cleaner fuels and the recent severe regulations on commercial fuel standards have pushed the need for innovative approaches to enhance the current industrial desulfurization technology. Nanotechnology is one such possible solution. $TiO_2$ and $MoO_3$ nanoparticles, however, appear to have the potential for industrial applications, whether used alone or in a multistage process with other adsorbents for desulfurization.

## CONFLICT OF INTEREST

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

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