A Review: Enhancement of Sulfur Removal From Crude Oil Using Nanomaterials

[1]Muhssn Hamzah Shamky, [2]Haider Zghair Jumaah,
[3]Talib Ali Ridha Elias, [4]Hussein Rashid Abood
[1,2,3,4] *Midland Refineries Company,*
Al-Daura Refinery
Baghdad, Iraq

[1]*Received: 11/05/2025; Accepted: 10/06/2025; Published: 13/06/2025*

Abstract

The sulfur compounds in crude oil poses significant environmental and industrial challenges, primarily due to the emission of harmful sulfur oxides (SOx) during fuel combustion, which contributes to acid rain and air pollution. Conventional desulfurization methods, hydrodesulfurization (HDS), have been widely used in petroleum refining; however, they often fall in removing refractory sulfur species such as thiophenes, dibenzothiophenes, and their alkylated derivatives under mild operating conditions. In recent years, nanotechnology has emerged as a transformative approach for enhancing desulfurization efficiency. This review presents a comprehensive analysis of the role of nanomaterials in improving sulfur removal processes from crude oil and its derivatives. Various classes of nanomaterials, including metal oxide nanoparticles (e.g., TiO_2, ZnO, and CeO_2), carbon-based nanostructures (e.g., carbon nanotubes, activated carbon), mesoporous materials, and metal–organic frameworks (MOFs), are critically reviewed for their adsorption and catalytic properties. .This review explores the current state of research on the application of nanomaterials for sulfur removal from crude oil. The persistent presence of sulfur compounds in crude oil poses substantial environmental and business challenges, more often than not because of the emission of harmful sulfur oxides (SOx) throughout gas combustion, which contributes to acid rain and air pollutants. Conventional desulfurization methods . Various types of nanomaterials—including metal oxides, carbon-based nanomaterials, and metal–organic frameworks (MOFs)—are examined for their mechanisms of action, performance metrics, and potential scalability. The review also addresses challenges such as stability, regeneration, and economic feasibility.

Keywords: *desulfurization; nanoparticles; crude oil; MOFs; sulphur emission*

1. Introduction

Crude oil includes lots of sulfur-containing compounds which includes thiols, sulfides, thiophenes, and their derivatives. These compounds are answerable for environmental pollutants and corrosion troubles in refining gadget. During combustion, sulfur is converted to sulfur oxides (SOx), contributing to acid rain and fitness hazards [1]. The maximum typically used technique for desulfurization within the petroleum industry is hydrodesulfurization (HDS), which operates underneath high temperature and strain, and requires high-priced hydrogen fuel and catalysts. However, HDS is less powerful in getting rid of refractory sulfur compounds like dibenzothiophene (DBT) and its alkylated derivatives. Nanomaterials have recently gained attention as **alternative desulfurizing agents** due to their high surface area, tunable surface chemistry, and unique physicochemical properties. This review summarizes the current progress in using nanomaterials for sulfur removal from crude oil and model fuels [2].

2. Sulfur In Crude Oil

Sulfur exists in crude oil mainly as [3]:

- Aliphatic thiols
- Aromatic thiophenes

[1] *How to cite the article:* Shamky M.H., Jumaah H.Z., Elias T.A.R., Abood H.R (June, 2025); A Review: Enhancement of Sulfur Removal From Crude Oil Using Nanomaterials; *International Journal of Advances in Engineering Research*, Vol 29, Issue 6, 15-20

- Benzothiophenes (BT)
- Dibenzothiophenes (DBT)

Refractory sulfur compounds like DBT are tough to take away due to their fragrant stability and steric limitation, necessitating alternative removal techniques beyond traditional HDS [2].

3. Nanomaterials in Desulfuriztion [4]

3.1 Adsorption Desulfurization (ADS)

Nanomaterials used in ADS function by selectively adsorbing sulfur compounds. Common materials include:

- Nano-ZnO: Shows high affinity closer to sulfur due to Lewis acid-base interactions.
- Activated carbon nanoparticles: Offer high floor location and can be modified with metals (e.g., Cu, Fe) to improve selectivity.
- Metal-natural frameworks (MOFs): Porous structures that can be functionalized to enhance selectivity.
- Zeolites (nano-sized): Nanocrystalline zeolites (e.G., Y, ZSM-5) are effective in capturing DBT.

For example: Soleimani et al. (2015) demonstrated 95% DBT removal using modified nano-ZnO at room temperature. And Zhao et al. (2018) used Fe-doped mesoporous silica nanoparticles with high DBT adsorption capacity (~150 mg/g)

3.2 Oxidative Desulfurization (ODS) [5]

Nanocatalysts boost up the oxidation of sulfur compounds into sulfones, which are then eliminated via extraction or adsorption. Materials used encompass:TiO_2 nanoparticles (photo-assisted or catalytically active)

- Nano-molybdenum oxides
- Perovskite-type nanocatalysts

Extractive and Photocatalytic Desulfurization

Some nanomaterials serve as both photocatalysts and extractants:

- Graphene oxide (GO) functionalized with ionic liquids can extract and oxidize sulfur compounds.
- TiO_2/graphene composites improve photocatalytic activity due to better electron mobility.

3.3 Advantages of Nanomaterial –Based Desulfurization [6]

- High floor vicinity allows greater active web sites for sulfur interaction.
- Tunability permits functionalization for selectivity towards specific sulfur species.
- Mild conditions lessen energy charges and environmental impact.
- Potential for regeneration and reuse in cyclic operations.

3.4 Nanomaterial Desulfurization Application [7]

Integration Into Refinery Units

Nanomaterials may be applied in numerous degrees of the refining process, frequently as improvements or dietary supplements to current gadgets:

A. Pre-treatment Units

Use: Nanomaterials (e.g., nano-adsorbents or catalysts) may be added inside the desalter or pre-hydrotreatment stage to reduce sulfur load earlier than entering high-priced hydrodesulfurization (HDS) gadgets.

Benefit : Extends catalyst existence in HDS gadgets and decreases hydrogen consumption.

B. Adsorptive Desulfurization Beds

Nanomaterials like ZnO, TiO_2, or doped activated carbon can be packed into adsorption columns.

Operation: Typically run at ambient to moderate temperatures (25–150°C) underneath atmospheric or slight pressure.

(IJAER) 2025, Vol. No. 29, Issue No. VI, June **e-ISSN: 2231-5152, p-ISSN: 2454-1796**

C. Polishing Step After HDS

For ultra-low sulfur gasoline (e.g., <10 ppm sulfur), nanomaterials may be used as a submit-HDS "sharpening" step to do away with ultimate refractory sulfur compounds like four,6-DMDBT.

4. Pilot-Scale And Emerging Technology

Refineries and research institutes have started pilot projects using nanomaterial-based approaches:

a. Oxidative Desulfurization (ODS) Units

- TiO_2 or MOF-based totally nanocatalysts can be deployed in oxidative reactors alongside oxidants like H_2O_2 or ozone.
- These can be modular units included in parallel with HDS or for distinctiveness product streams (e.g., jet fuel, marine fuel).

b. Nano-Coated Catalytic Beds

Some companies are testing existing hydroprocessing units retrofitted with nanostructured catalyst supports to increase surface area and sulfur removal efficiency).

5. Product-Specific Applications [8]

A. Diesel Fuel

- Diesel incorporates heavy and sterically hindered sulfur compounds.
- Nano-adsorptive or oxidative desulfurization is useful right here, particularly in producing Ultra Low Sulfur Diesel (ULSD).

B. Gasoline and Naphtha

Lower severity processes are best here to keep away from octane loss.

Nanomaterials offer selective desulfurization with out affecting octane-wealthy aromatics, in contrast to conventional HDS.

C. Jet Fuel and Marine Fuels

- For excessive-performance fuels, easy-burning houses are critical.

Nano-ODS structures are gaining attention for selective and mild desulfurization.

6. Pore Size And Distribution Of Pore Size [9]

Lower Hydrogen Use: Nanomaterial techniques often function with out hydrogen, saving electricity and lowering CO_2 emissions**.**

- **Energy Savings:** Operate at lower temperatures and pressures than conventional HDS.
- **Regenerability**: Many nano-adsorbents and catalysts may be regenerated through simple thermal or chemical methods.

7. Performance Of Membrane [10]

- **Material Stability:** Some nanomaterials may degrade beneath actual-world refinery conditions (temperature, contaminants).
- **Cost of Production:** Though less expensive over time, initial charges for excessive-purity nano-catalysts or adsorbents may be high.
- **Separation/Recovery:** Fine nanoparticles need to be immobilized or based to keep away from loss within the gas flow.
- **Scale-Up:** Moving from lab-scale to industrial-scale stays a prime hurdle, though established supports and composite materials help.

8. Future Researches

Selective Targeting of Refractory Sulfur Compounds

- Design nanomaterials with tailored pore sizes, surface chemistry, or functional groups to selectively remove complex compounds like 4,6-DMDBT.
- Employ molecular imprinting or smart recognition-based materials.

Integration with Existing Technologies

- Combine nanomaterials with conventional hydrodesulfurization (HDS) or oxidative desulfurization (ODS) for hybrid processing units.
- Study synergistic effects under industrial operating condition

9. Conclusions

Nanomaterials provide a promising path for enhancing sulfur removal from crude oil and petroleum fractions under environmentally friendly and cost-powerful situations. Their specific floor and chemical homes offer a possible course to triumph over the restrictions of traditional techniques. Continued research in synthesis, functionalization, and system integration may be key to bringing those technologies closer to business deployment. nanomaterials offer a versatile and efficient platform for next-generation desulfurization technologies. Future efforts should aim to optimize synthesis techniques, enhance material stability under operating conditions, and develop hybrid systems that maximize sulfur removal efficiency while minimizing cost and environmental impact.

Nanomaterials hold actual promise for boosting desulfurization in refineries by way of supplementing or partly replacing strength-intensive techniques like HDS. Applications variety from pre-remedy and sprucing steps to full stand-on my own structures for specific gas cuts. While demanding situations remain in scaling and integration, ongoing R&D and pilot trials show significant potential for these technologies to support cleaner fuel production in the near future.

10. Conflict of Interest

The authors declare that they have no conflict of interest.

11. Funding Declaration

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

12. References

Ahmad, W., Ur Rahman, A., Ahmad, I., Yaseen, M., Mohamed Jan, B., Stylianakis, M. M., Kenanakis, G., & Ikram, R. (2021). Oxidative desulfurization of petroleum distillate fractions using manganese dioxide supported on magnetic reduced graphene oxide as catalyst. *Nanomaterials, 11*(1), 203. https://doi.org/10.3390/nano11010203

Al Khazraji, A. H., Mohammed, M. K., Fahmi, A. H., & Mourad, S. H. (2024). Removal of sulfur compounds from Iraqi crude oil using γ-Al_2O_3 nanoparticles. *Bulletin of the Chemical Society of Ethiopia, 38*(5), 1241–1250.

Radhi, A. (2023). Comparison of the efficiency of titanium and molybdenum nanometal oxides as adsorbents for sulfur compounds in crude oil. *Journal of Nanostructure in Chemistry, 13*(1), 1–9.

Sadare, O. O., & Akinmoladun, F. A. (2017). Biodesulfurization of fossil fuels: Analysis and perspectives. *F1000Research, 6*, 1116. https://doi.org/10.12688/f1000research.133427.1

Soleimani, M., & Moghaddam, A. Z. (2015). Desulfurization of fuel oil using nano-ZnO. *Fuel Processing Technology, 135*, 240–246. https://doi.org/10.1016/j.fuproc.2014.12.021

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today, 86*(1), 211–263. https://doi.org/10.1016/S0920-5861(03)00412-7

Srivastava, V. C. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances, 2*(3), 1015–1033. https://doi.org/10.1039/C1RA00309G

US Environmental Protection Agency (EPA). (n.d.). *ULSD Standards*.

Wang, H., Liu, S., Zhang, L., & Li, Y. (2017). TiO_2-based photocatalysts for oxidative desulfurization of model fuels. *Energy & Fuels, 31*(3), 2053–2060. https://doi.org/10.1021/acs.energyfuels.6b02182

Zhao, D., Liu, R., Wang, J., & Liu, B. (2018). Fe-doped mesoporous silica nanoparticles for efficient adsorptive desulfurization. *Chemical Engineering Journal, 334*, 1301–1310. https://doi.org/10.1016/j.cej.2017.11.062

About Authors

Muhssn Hamzah Shamky is a qualified production and metallurgy engineer with a Bachelor of Science degree from the University of Technology, Baghdad, earned in 1997. He has extensive experience in engineering inspection and project management within the oil refining industry, particularly with the Midland Refineries Company (M.R.C) at the Al-Daura Refinery. Mr. Shamky holds professional certification in non-destructive testing in accordance with the American Society for Non-Destructive Testing (ASNT – TC – 1A) standards. His qualifications include ASNT Level II certifications in magnetic particle inspection; liquid penetrant inspection; and visual inspection.

Throughout his career, he has served in various key technical and operational roles. He has worked as an Inspector Engineer in the Engineering Inspection Department of M.R.C and has been actively involved in the Boilers and Furnaces Department under the Maintenance Board. Additionally, he has contributed to the Follow-up Projects Department of the Exterior Refineries Board and held positions in the Studies and Planning Department under the Technical & Engineering Board. Currently, he is serving in the Project Management Department of the Technical & Engineering Board at M.R.C. His combined technical expertise and hands-on experience have made him a valued contributor to the refinery's operational and strategic initiatives.

Haider Zghair Jumaah Al-Geraani, is a seasoned mechanical engineer with over three decades of experience in the oil refining industry. He currently serves as a Senior Chief Engineer in the Project Management Department of the Ministry of Oil – Midland Refinery Company. Mr. Al-Geraani began his career in 1993 at the Daura Refinery, where he worked in the Mechanical & Maintenance Department as a sub-supervisor responsible for the repair and maintenance of rotary equipment such as pumps; steam turbines; and compressors. Over the years, he steadily advanced through various positions—becoming Supervisor in 2000; Assistant Engineer in 2001; Engineer in 2003; Senior Engineer in 2005; Assistant Chief Engineer in 2008; and Chief Engineer in 2012. In 2016, he became Head of the Pump Shop Section in the Rotating Equipment and Workshops Department, and in 2019, was promoted to First Deputy Manager of the same department. In 2021, he moved to the Studies and Development Department, serving as Chief Engineer and later Senior Chief Engineer. Since 2023, he has been working in the Project Management Department in the same senior capacity.

Mr. Al-Geraani holds a Diploma in Mechanical Engineering with a specialization in Pumps and Turbines from the Iraqi Oil Training Institute (1993), and a Bachelor's degree in Mechanical Engineering from the University of

(IJAER) 2025, Vol. No. 29, Issue No. VI, June **e-ISSN: 2231-5152, p-ISSN: 2454-1796**

Technology, Baghdad (2001). He also received TOT (Training of Trainers) certification from the Ministry of Oil in 2018. An expert in the maintenance of rotary equipment, Mr. Al-Geraani has been training engineers and technicians at the Iraqi Ministry of Oil, the Iraqi Oil Training Institute, and the Arab Petroleum Training Institute since 2005. He has participated in numerous technical and leadership training programs across Iraq; Portugal; Egypt; India; the United States of America; and Jordan. Fluent in Arabic and proficient in English, he is recognized for his technical acumen, dedication to capacity building, and long-standing contributions to Iraq's oil industry.

Talib Ali Ridha Elias, based in Baghdad, Iraq, is an experienced mechanical engineer with a strong background in the oil refining industry, particularly in the maintenance and management of rotating machinery. He began his career in 2000 as an Assistant Engineer at the North Refineries Company, where he was responsible for maintaining pumps and compressors. In 2003, he was appointed Head of the Maintenance Section at External Refineries, and by 2005, he joined Midland Refineries Company in the Maintenance Authority of the Rotating Equipment and Workshops Department. Over the years, he rose through the ranks, becoming a Senior Engineer in 2010 and Head of the Engineering Supplies Section in 2016. His leadership and technical expertise led to his appointment as Deputy Manager of the Rotating Machinery Department in 2019, and in 2020, he was promoted to the position of Senior Chief Engineer. He later contributed to the Studies and Development Department in 2021 and has been serving in the Project Management Department since 2023.

Mr. Elias holds a Bachelor's Degree in Mechanical Engineering with a general specialization from the University of Mosul. He has also completed numerous specialized training programs, including courses in programming and leadership, further strengthening his skills in engineering project execution and departmental coordination. With over two decades of experience, Mr. Elias is recognized for his technical proficiency, leadership capabilities, and continued service to Iraq's refining sector.

Hussein Rasheed Abbood, is a seasoned engineering professional with over 25 years of experience in the manufacturing and erection of oil and gas equipment. He serves as a Senior Chief Engineer; Projects Manager at the Ministry of Oil; Mid Land Refinery Company. He holds a Bachelor's degree in Chemical Engineering from Baghdad University; 1993, and a Higher Diploma in Oil Refinery and Gas Technology; 2015. Throughout his career, Mr. Abbood has held several key positions at HEESCO Company, including Production Engineer (1999–2001); Planning Engineer (2002–2004); and Projects Manager for various sites in Iraq (2005–2008). He later became the Chief of the Preparation Division (2008–2011) and then the Chief of the Technical Division (2012–2019) of the steam boilers factory. From 2020 to 2023, he led the Haditha Refinery Project as its Projects Manager. He also holds several professional certifications, including certificates in welding methods and techniques; project management; and quality control auditing.