



Industrial adsorption methods for reduction of sulphur content in hydrocarbon streams

Fazil Rahimli*

PhD in Petrochemistry
Azerbaijan State Oil and Industry University
AZ1010, 20 Azadliq Ave., Baku, Azerbaijan
<https://orcid.org/0009-0006-3970-308X>

Nigar Mamedova

PhD, Associate Professor
Azerbaijan State Oil and Industry University
AZ1010, 20 Azadliq Ave., Baku, Azerbaijan
<https://orcid.org/0000-0001-8508-8192>

Abstract. Industrial adsorption methods for reducing sulphur content in hydrocarbon streams were investigated with an emphasis on their engineering efficiency and technological adaptability in oil refineries. A comparative analysis of the use of zeolites, activated carbons, metal-organic frameworks, carbon molecular sieves, metal oxides, polymeric materials, metal sulphides, modified clay and bentonite aimed at reducing the sulphur content in hydrocarbon streams was conducted. Adsorption using zeolites and metal-organic frameworks was noted to be highly effective in removing sulphur-containing compounds such as thiophenes and mercaptans, especially at high sulphur concentrations. However, these methods require significant capital expenditure and a complex infrastructure to scale. Activated carbons, despite their availability and cost-effectiveness, have demonstrated lower efficiency in removing sulphur from heavy hydrocarbons and limited regeneration capabilities. Hybrid methods that combine adsorption with catalytic desulphurisation have proven to be promising for deep sulphur removal and lower operating costs due to the ability to regenerate the adsorbent. For large plants, hybrid technologies and methods using zeolites and metal-organic frameworks are optimal, providing high efficiency while meeting environmental standards. For small and medium-sized refineries, activated carbon technologies are economically viable. Thus, the choice of adsorption method depends on the specifics of the enterprise, the type of hydrocarbon flow and the opportunities for introducing innovative technologies

Keywords: zeolites; organometallic scaffolds; catalytic desulphurisation; oil refineries; activated carbons

Introduction

Reduction of sulphur content in hydrocarbon streams is the most important task of the refining industry due to strict environmental standards and the need to improve fuel quality. High sulphur content in petroleum products not only deteriorates their performance characteristics but also contributes to environmental

pollution, which leads to additional economic and environmental risks. One of the most effective methods of removing sulphur-containing compounds is adsorption, which is used to purify hydrocarbon streams at various refining stages. In 2023, the development of new and improvement of existing adsorbents, such as zeolites,

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activated carbons and metal-organic frameworks, as well as combined methods combining adsorption with catalytic desulphurisation were prioritised (Yang *et al.*, 2023). However, the choice of the most effective method depends on many factors, including the type of feedstock to be treated, sulphur concentration and technical features of the plant.

Q. Shi & J. Wu (2021) investigated the use of zeolites in the adsorption processes of sulphur-containing compounds, noting their high efficiency at high sulphur concentrations. These materials significantly improved the quality of hydrocarbon streams and met environmental standards. G. Li *et al.* (2024) analysed the use of activated carbons for sulphur removal, pointing out their availability and economic benefits. However, they emphasised that for heavier hydrocarbon fractions, this method had limited effectiveness. B. Saha *et al.* (2021) studied metal-organic frameworks as a promising material for sulphur adsorption with high selectivity and modification ability. However, the work pointed out that the high cost of organometallic frameworks made them inappropriate for mass application in large refineries. Y. Pan *et al.* (2024) emphasised the problems of adsorbent regeneration, which was an important aspect of the long-term operation of these materials in industrial conditions. They emphasised that the possibility of regeneration significantly increased the economic attractiveness of adsorption technologies.

X. Wang *et al.* (2024) considered the removal of asphalt-resin-paraffin deposits by chemical methods in the production of highly paraffinic oil. The authors optimised the chemical method of oil well remediation by proposing a technique for selecting the most effective reagent, stressing the importance of an individual approach for each specific case. Jumina *et al.* (2021) investigated the combination of adsorption and catalytic desulphurisation, confirming their high efficiency in sulphur removal. They also observed that such methods could reduce operating costs by reducing the need for frequent replacement or regeneration of adsorbents. S.A. Ganiyu & S.A. Lateef (2021) emphasised the advantages of combined technologies that provided deep hydrocarbon purification and minimised waste. They argued that such approaches could significantly improve the economic efficiency of refineries.

K. Taghaddom *et al.* (2023) identified the high level of capital cost in implementing advanced refining technologies, which was a serious constraint for Small and medium-sized enterprises (SMEs). They also investigated possible ways to optimise the cost when using activated carbon for biomass degassing, highlighting the importance of selecting an efficient adsorbent and process parameters to maximise profitability. W. Zhang *et al.* (2022) investigated the environmental aspects of adsorption applications, emphasising the need to select methods that minimise emissions and waste during the purification of hydrocarbon streams. Their study

emphasised meeting environmental standards and regulatory requirements. H.A. Al-Jamimi *et al.* (2022) proposed a hybrid approach using the support vector method (SVM) and genetic algorithm (GA) to treat hydrocarbons from sulphur. These minimised the sulphur content, SO₂ emissions and hydrodesulphurisation costs and achieved purification efficiency. The authors also emphasised the benefits of complying with strict environmental regulations. However, a comprehensive analysis of all existing adsorption methods concerning economic feasibility and technological adaptability in large and small refineries was lacking among scientific papers, which requires further research.

The study aimed to evaluate and compare different industrial adsorption methods in terms of their applicability for reducing sulphur content in hydrocarbon streams in refineries, with a particular focus on the engineering aspects and the possibility of integrating these methods into existing processes.

Materials and Methods

The study addressed the situation in Azerbaijan, which is determined by the availability of significant reserves of raw materials to produce zeolites and a developed oil and gas industry, where adsorbents are widely used. Four main industrial adsorption methods used to reduce sulphur content in hydrocarbon streams were analysed: adsorption on zeolites, the use of activated carbons, metal-organic frameworks (MOFs) and hybrid methods combining adsorption with catalytic desulphurisation. Sulphur compounds, commonly found in the feedstock supplied to oil refineries, were analysed: thiophenes, mercaptans and hydrogen sulphide.

The methods of using zeolites, activated carbons, metal-organic frameworks, carbon molecular sieves, metal oxides, metal sulphides, modified clays and bentonites, as well as hybrid technologies and polymeric materials that demonstrate the effectiveness of removing sulphur compounds under various technological conditions were considered. Each method was evaluated for its effectiveness in removing sulphur from hydrocarbon streams. The conditions under which the methods are most effective were determined. An important aspect of the analysis was the influence of various parameters, such as temperature, pressure and hydrocarbon stream composition. This was used to identify which methods provide the best results for the removal of light sulphur compounds and which are more effective for the removal of complex contaminants such as heavy hydrocarbons.

As part of the analysis of the economic feasibility of each method, the capital costs of equipment installation and operation, the cost of adsorbent regeneration, and the cost of replacing them during operation were estimated. The analysis of the availability of raw materials, durability and cost of adsorbent production was prioritised. This was used to identify the most

cost-effective methods for large refineries, as well as for small and medium-sized enterprises that may face a lack of financial resources. The scalability of the methods was also an important aspect of the study. The possibility of implementing these technologies at different stages of production, from small installations to large production facilities, was assessed. The integration of the methods into existing refinery process chains, a significant aspect in terms of equipment modernisation and process optimisation, was analysed. The peculiarities of each technology in terms of implementation in real operation were addressed as well.

An important part of the study was the sustainability of the selected methods and their environmental impact. This analysis analysed the possibility of adsorbent regeneration, which reduces the amount of waste and reduces the cost of replacing adsorbents during operation. The extent to which each method affects the ecosystem was also investigated, addressing the long-term operation of the equipment and the possible environmental risks associated with the use of these technologies.

The study also developed recommendations for refineries on the selection of optimal adsorption methods. For this purpose, the needs of large and small refineries were analysed, as well as possible ways to improve existing desulphurisation processes. The recommendations cover both technical characteristics as well as economic and environmental aspects aimed at optimising processes, addressing all factors affecting refinery efficiency and long-term sustainability.

Results

Adsorption of sulphur-containing compounds is crucial for the purification of hydrocarbon streams, providing a reduction in sulphur emissions and improving the quality of the fuel produced. High sulphur content in hydrocarbons not only degrades their performance characteristics but also contributes to increased emissions of toxic compounds into the atmosphere. Therefore, the main objective of adsorption is to improve the quality of fuel. In the process of sulphur removal, fuel performance is significantly improved: the harmful effect on engines is reduced, the service life of equipment is increased, and operating costs are reduced. In addition, improvement of fuel quality leads to its more efficient utilisation, which contributes to saving energy resources and reducing the cost of hydrocarbon materials processing.

In the adsorption process, sulphur compound molecules adsorb on the surface of the adsorbent material, which significantly reduces the concentration of sulphur in the fuel. This method of sulphur removal is highly efficient, which allows the production of fuel following the environmental standards Euro-5, Euro-6 and Azerbaijan standards (Griffiths, 2023). To ensure compliance of the implementation of adsorption technologies with international standards, as well as to minimise emissions and comply with environmental regulations, the

company needs an environmental management system. The basis for its development and implementation is provided by ISO No. 14001 (2015) standard, with the help of which the requirements for fuel quality, norms of sulphur level reduction to minimum values, and methods of adsorbent selection are established. For instance, biochar is an effective and inexpensive means of removing gaseous pollutants from combustion flue gases, including SO₂ and volatile organic compounds. It is a cheaper alternative to solid sorbents such as activated carbon, zeolites, carbon nanotubes, carbon molecular sieves and metal-organic frameworks (Wen *et al.*, 2023).

Adsorption on zeolites is one of the most effective methods of purification of hydrocarbon streams from sulphur-containing compounds. Zeolites have a unique microporous structure, which can be used to provide high selectivity to various sulphur-containing substances, such as thiophenes and mercaptans (Lee & Valla, 2019). These substances are major contaminants in hydrocarbon streams, and their removal by zeolites significantly improves fuel quality. The selectivity of zeolites to thiophenes and mercaptans is due to their size, polarity and structural feature, which allows effective retention of molecules of these compounds on the adsorbent surface (Pérez-Botella *et al.*, 2022). An important advantage of zeolites is their ability to regenerate. After saturation of the adsorbent with sulphur-containing molecules, it can be subjected to the regeneration process, restoring its adsorption properties. Depending on the type of adsorbent, it can be regenerated 3-10 times: activated carbon up to 5 times, biochar and metal-organic frameworks up to 10 times, provided the optimum conditions are met. This reduces operating costs, allowing the adsorbent to be reused many times without the need to replace it. Regeneration of zeolites is usually carried out by a thermal method, which removes all accumulated contaminants and returns the material to its original state. This process is a key factor in making the use of zeolites in industry more economically attractive.

However, there are several limitations in the use of zeolites. One of them is a decrease in adsorption efficiency at high sulphur concentrations in hydrocarbon streams (Chai *et al.*, 2021). In such conditions, the zeolite can be saturated quickly, which leads to the need for frequent regeneration or replacement of the material. Zeolites are also susceptible to contaminants, such as particulate matter or other organic matter, which can block the pores and reduce the overall efficiency of the adsorption process. These limitations need to be addressed in designing treatment systems to ensure stable operation of the adsorption unit under variable loads and hydrocarbon stream composition.

Activated carbons are one of the most popular and economically available materials for the removal of sulphur-containing compounds from hydrocarbon streams. This adsorption method is suitable for the removal of

hydrogen sulphide (H_2S) and light sulphur compounds such as alpha-methylthiophene or methylmercaptans. Due to their highly porous structure, activated carbons provide a large surface area for adsorption, rendering them effective for the adsorption of gas or soluble sulphur-containing molecules, especially in the early stages of the purification process (Paucar *et al.*, 2021).

One of the main advantages of activated carbons is their economic availability. The material has a relatively low cost and is available in various forms, which can be used in a wide range of industrial processes. Activated carbons, in contrast to organometallic frameworks and zeolites, are used in cases where sulphur purification depth requirements are less stringent, such as in small or medium-sized plants where savings on capital investment are key. This may apply to cases such as treating a hydrocarbon stream with sulphur content as low as 500 parts per million (ppm), which meets less stringent requirements than for deep purification requiring significant investment in higher quality adsorbents such as metal-organic frameworks, which can operate effectively at sulphur contents as low as 10-50 ppm. In such cases, activated carbons can perform effectively despite their higher tendency to saturate, making them an attractive choice if purification depth requirements do not exceed 500-1,000 ppm. This is also true for processes where economic efficiency is more important than ultra-purification. However, despite the economic benefits, the use of activated carbons has several limitations. One of them is their low efficiency in the treatment of heavy hydrocarbon streams. For the removal of sulphur from heavy oil fractions, activated carbons do not always provide the required degree of purification, as their porous structure may not be able to cope with large molecules or high concentrations of contaminants. In addition, the regeneration process of activated carbons is labour-intensive and expensive. Due to the saturation of the adsorbent with sulphur-containing compounds, the process of regenerating the adsorbent requires significant energy and time, which increases operating costs. In most cases, activated carbons lose part of their adsorption capacity after several regeneration cycles, which leads to the need for their frequent replacement.

MOFs are innovative materials that have attracted much attention due to their high selectivity in the adsorption of various sulphur-containing compounds. These materials are composed of metals bonded with organic ligands, which provides them with unique porous structures with a large surface area. MOFs can select and adsorb specific molecules such as thiophenes, mercaptans and other sulphur-containing organic compounds, making them extremely effective for sulphur purification of hydrocarbon streams. Their high selectivity allows achieving a significant reduction of sulphur concentration with relatively low energy and time consumption for the purification process (Yu *et al.*, 2024).

One of the main advantages of MOFs is the ability to modify their structure depending on the specific needs of the refinery. The porous structure of these materials can be adapted by changing the type of metals or organic ligands, which can be used for optimised adsorption properties for specific types of hydrocarbon streams. This flexibility makes MOFs promising for creating customised solutions, which is especially important when dealing with different types of oil and gas. In contrast to traditional adsorbents such as activated carbons or zeolites, MOFs open new opportunities for improving treatment efficiency and reducing costs.

However, despite their advantages, the use of MOFs faces several limitations. One of the main factors is the high cost of these materials. The production of MOFs requires complex synthetic processes and expensive starting materials, which makes their use expensive, especially in large-scale production where significant amounts of adsorbents are required. In addition, MOFs have low stability in aggressive industrial environments such as high temperatures, humidity and the presence of various contaminants. Therefore, in refineries, these materials can lose their effectiveness due to structural degradation, which limits their durability and requires additional replacement or regeneration costs.

Carbon molecular sieves (CMS) are an important component of modern hydrocarbon stream treatment technologies. Their application covers a wide range of refinery and gas industry applications, as they reduce sulphur compounds to environmental standards. CMS demonstrates high efficiency in the removal of hydrogen sulphide, thiols and light mercaptans from natural gas and hydrocarbon streams (Nezhad *et al.*, 2023). For instance, they are used in feedstock pretreatment stages, where adsorbents placed in columns or reactors reduce the sulphur content before the main refining processes. This not only improves feedstock quality but also protects subsequent stages from contamination.

In large refineries, hydrotreating is the standard method for desulphurisation of heavy fractions such as diesel and petrol. CMS can be used as a supplement, providing fine purification after the main treatment. This is particularly important for achieving ultra-low sulphur concentrations, making them indispensable to produce high-quality petroleum products. Hydrogen used in hydrotreating can contain hydrogen sulphide, which contaminates the catalysts. CMS effectively remove these compounds, increasing the productivity and durability of the equipment.

CMS offers several key advantages. They are flexible in terms of customisation to specific streams and compounds, environmentally friendly as they meet Euro 5 and Euro 6 standards, and cost-effective due to reduced catalyst wear and regeneration capabilities. These characteristics make them a competitive solution for modern refineries. Nevertheless, there are technical limitations: large volumes of adsorbent are

required to process large volumes of feedstock, which increases costs. In addition, wear and tear during regeneration cycles and extreme conditions at some refining stages require additional solutions.

Hybrid methods, combining adsorption and catalytic desulphurisation, represent an innovative strategy for deep sulphur removal from hydrocarbon streams. This approach combines the advantages of the two processes: adsorption effectively removes sulphur-containing substances such as thiophenes and mercaptans, while catalytic desulphurisation breaks down more complex sulphur compounds into less harmful substances. The combined use of adsorption and catalysis techniques can provide deeper purification of hydrocarbons, allowing sulphur levels to be achieved to meet the most stringent environmental standards. For instance, the Euro-6 standard for automotive fuels requires a sulphur content of no more than 10 mg/km, which is significantly lower compared to less stringent standards such as Euro-5, where the allowable sulphur level is 50 mg/km. Such low sulphur levels can be achieved by using advanced technologies, such as hybrid methods, and more efficient adsorbents that provide purification at a deeper level. This combination of processes is particularly effective when dealing with heavy hydrocarbons where standard purification methods are insufficient (Hassan *et al.*, 2022).

One of the key advantages of hybrid methods is increased cost efficiency, due to the possibility of regeneration of both adsorbent and catalytic material. Materials such as activated carbon, zeolites, carbon molecular sieves and metal-organic frameworks are often used for adsorption of sulphur-containing compounds. These adsorbents effectively remove sulphur in the purification stage of hydrocarbon streams and can be subjected to multiple regeneration. Catalysts

used for catalytic hydrodesulphurisation are metal oxides (e.g., vanadium oxides, molybdenum oxides), metal sulphides and aluminosilicates, which promote a chemical reaction that removes sulphur from hydrocarbons at high temperatures and pressures. Importantly, both adsorbents and catalysts can be regenerated, significantly reducing operating costs and improving the durability of the purification process. The regeneration of adsorbents allows for 3-10 times of use, depending on the type of material and process conditions. Catalytic materials, such as sulphides and metal oxides, can be recovered 3-5 times using thermal or chemical methods (Ismailov & Gashimov, 2010). The combination of these processes not only improves fuel quality but also reduces long-term operating costs for hydrocarbon treatment.

However, the use of hybrid methods also has its limitations. One of the main obstacles is the difficulty of implementing such technologies into the existing refinery infrastructure. Integrating adsorption with catalytic desulphurisation requires complex equipment upgrades as well as staff training, which can require significant capital expenditure. In addition, such systems require fine-tuning of the processes to ensure their synchronised operation and avoid a reduction in overall purification efficiency. As a result, despite the high potential of hybrid methods, their implementation can be difficult, especially in the case of the limited financial and technological capabilities of the enterprise. Refiners face a variety of factors when selecting technologies for removing sulphur from hydrocarbon streams, including the efficiency, cost-effectiveness, scalability and sustainability of the methods used (Table 1). Each of the existing technologies has its strengths and weaknesses that must be assessed in the context of the specific operating conditions of the refinery.

Table 1. Comparative analysis of adsorption methods

Method	Sulphur removal efficiency (ppm)	Economic profitability	Scalability	Regeneration capability (times)	Suitable petroleum products
Zeolites	10-50	High	High	5-6	Light hydrocarbon flows
Activated carbons	50-100	Average	Average	2-3	As a supplement in hydrotreating
Metal-organic frames	<10	Low	High	5-6	For high-purity products
Hybrid methods	<10	Average	Average	3-4	For the fine purification of heavy hydrocarbons
Carbon molecular sieves	<10	Average	High	4-5	For high-purity products
Metal oxides	<10	High	High	5-6	Light hydrocarbon flows
Polymeric materials	10-20	Average	Average	1-2	As a supplement in hydrotreating
Metal sulphides	10-50	High	Average	2-3	Light hydrocarbon flows
Modified clays and bentonites	10-50	High	High	3-4	Light hydrocarbon flows and diesel

Source: compiled by the authors based on V.C. Srivastava (2012)

Methods based on the use of metal-organic frameworks and hybrid technologies show the best results in terms of efficiency. MOFs are highly selective and can be used to effectively remove sulphur-containing compounds, even at high sulphur concentrations, such as those found in primary and secondary refining stages such as hydrotreating and hydrodesulphurisation. High levels of sulphur are often encountered in these stages, requiring effective purification methods. Hybrid methods, combining adsorption with catalytic desulphurisation, can be effectively applied to hydrotreating and hydrodesulphurisation in refineries. For instance, in the hydrotreating stage of diesel or petrol where sulphur-containing compounds are in high concentrations, the use of hybrid methods can provide deep purification and high sulphur removal rates, reducing the need for continuous replacement of adsorbents and catalysts. It also helps maintain process stability under high temperature and pressure conditions. Activated carbons and zeolites are effective in the purification of hydrocarbons from sulphur, but their effectiveness is limited at high sulphur concentrations (greater than 1-2%) or complex sulphur-containing compounds such as thiophenes. Under such conditions, MOFs and carbon molecular sieves are more effective, providing better selectivity and high capacity.

Cost-effectiveness is essential, especially for businesses with limited budgets. Activated carbons are a more affordable option due to low material costs and ease of implementation. This solution is ideal for smaller refineries or temporary situations, such as equipment refurbishment or short-term peaks, where full modernisation of sulphur treatment processes is not feasible. While MOFs and hybrid methods offer high efficiency, their cost and complexity of implementation can be significant, making them less economical in the short term. However, when considering the long-term benefits of improved fuel quality and compliance with environmental standards, more expensive methods may justify the investment.

Scalability is also an important criterion, especially for large refineries where large volumes of hydrocarbons need to be processed. Zeolites and MOFs have a high potential for scalability. This makes them promising for large plants where methods capable of operating efficiently at high flow volumes are required. These technologies offer high levels of purification

down to sulphur levels, for instance, in the range of 10-50 ppm, making them attractive to large plants that need to meet stringent environmental standards and handle more complex hydrocarbon streams. Adoption of technologies such as catalytic hydrodesulphurisation requires significant capital investment, which can range from USD 5 to USD 10 million, depending on the scale and complexity of the plant. This limits their use to small refineries that cannot justify such costs. Small refineries typically have a capacity of up to 50,000 barrels of oil per day and are limited in resources. These facilities often opt for more affordable and easily scalable technologies, such as adsorption using activated carbons. These techniques allow the solution to be quickly integrated into existing systems without significant installation and maintenance costs.

The sustainability of technological solutions is important for long-term application. Hybrid technologies, which combine adsorption and catalytic desulphurisation, are the most environmentally friendly option, as they allow for the reuse of adsorbents and catalysts, which reduces waste and minimises environmental pollution. This approach contributes to the overall sustainability of the process. MOFs, despite their high efficiency, require further research to optimise their stability and durability in industrial applications. This limits their widespread use, although their sustainability prospects remain promising. Activated carbons, although easily regenerated, can pose environmental problems due to the need for frequent replacement and disposal of the material.

Thus, the choice of method for sulphur removal from hydrocarbon streams depends on many factors. For large refineries focused on high efficiency and scalability, MOFs or hybrid methods are preferred. For plants with limited financial resources or those that need to implement solutions quickly, activated carbons will be more suitable. The choice should be based on a comprehensive assessment of all factors, including efficiency, cost, scalability and environmental sustainability of the technologies (Cako *et al.*, 2022). Technological adaptability is a key factor in the selection of sulphur removal methods for refineries, as the successful integration of new technologies must address both economic viability and environmental standards (Table 2). In this context, scalability, integration into existing processes and environmental sustainability are important aspects.

Table 2. Technological adaptability of adsorption methods

Aspect	Zeolites	Activated carbons	Metal-organic frames	Hybrid methods
Integration	Complex	Simple	Complex	Average
Environmental sustainability	Moderate	Limited	High	High
Initial costs	Average	Low	High	Average
Sulphur-containing substances	Hydrogen sulphide, organic sulphur-containing compounds	SO ₂ , hydrogen sulphide, volatile organic compounds	SO ₂ , volatile organic sulphurous compounds	SO ₂ , hydrogen sulphide, organic compounds

Source: compiled by the authors based on K. Chen *et al.* (2020)

The integration of new technologies into existing processes is another key aspect. Activated carbon, due to its relatively low cost and ease of use, can be easily integrated into existing treatment systems. This technology does not require fundamental process changes, which greatly simplifies its implementation and reduces the capital cost of modernisation. In the case of zeolites and MOFs, the integration process may require not only significant financial investment but also a redesign of some equipment, making their application complex and requiring careful preparation. Thus, for plants that already have functioning plants, activated carbons are a better option in terms of technological adaptability.

Environmental aspects are substantial in the long-term sustainability of technologies. In the face of increasing environmental demands, adsorbent recovery is becoming an important mechanism for reducing waste and increasing material efficiency. Hybrid methods that combine adsorption with catalytic desulphurisation have significant environmental potential, as they allow for multiple regeneration of adsorbents and catalysts, thus reducing waste. Activated carbons, although they have limitations in terms of regeneration frequency, such as reduced efficiency with multiple regenerations and possible accumulation of contaminants in the porous structure, can also reduce environmental impacts due to the possibility of material reuse. These limitations relate to the loss of adsorption capacity and the need to use additional methods, such as thermal or chemical regeneration, to maintain their efficiency at the required level. While MOFs, despite their high efficiency, require further research in terms of their sustainability and regeneration, which limits their widespread use in industrial plants.

Thus, when choosing technologies for removing sulphur from hydrocarbon streams of refineries, it is necessary to consider their technological adaptability. For large enterprises with the possibility of significant capital investments, it is advisable to introduce more efficient but expensive technologies, such as zeolites and MOFs. For smaller or temporary solutions, methods that can be easily integrated into existing systems, such as activated carbons, are more suitable, especially if the focus is on cost optimisation and minimising environmental impact.

With environmental standards constantly evolving and the desire to improve fuel quality, refineries are faced with the need to select effective technologies for sulphur removal from hydrocarbon streams. Recommendations for selecting adsorption methods for such plants depend on a variety of factors, including refinery size, technical capabilities and financial resources. For large refineries, hybrid methods or metal-organic frameworks are appropriate. These require significant upfront costs but provide high sulphur removal efficiencies to achieve the desired environmental standards even when treating complex hydrocarbon streams.

Hybrid systems incorporate adsorption and catalytic desulphurisation to provide deep purification, making them attractive to large plants with long-term environmental and economic goals. At the same time, MOFs can be used to optimise purification due to their high selectivity and ability to be modified to suit specific refinery conditions.

Activated carbons are suitable for smaller refineries, those with limited financial resources, and for a quick or temporary solution to a treatment problem: they are low-cost, easy to use and readily available. Although activated carbons are not as effective for deep removal of sulphur in complex hydrocarbons, they can be used for pretreatment, making them a good option for refineries that cannot afford to implement more expensive technologies.

The choice of technology should be preceded by an analysis of economic viability and environmental compliance. It is necessary to address the cost of installation and operation of technologies, their durability, the possibility of material regeneration, and the impact on the environment. Therefore, refineries should select technologies with a view to long-term benefits, optimising costs and achieving maximum efficiency in the treatment of hydrocarbon streams from sulphur.

Discussion

The study determined that adsorption methods demonstrate high efficiency for removing sulphur compounds from hydrocarbon streams, but each technology has its limitations. Activated carbons, despite their effectiveness in removing sulphur, are limited in their application at high sulphur concentrations in the stream and are sensitive to heavy hydrocarbon contamination. This limits their use in complex hydrocarbon streams.

Zeolites are reliable adsorbents due to their selectivity to thiophenes and mercaptans. B. Bulut *et al.* (2022) conducted studies on LPG desulphurisation using modified zeolites. These zeolites were treated with metal ions (Cu^{2+} , Zn^{2+} and Cu^{2+} - Zn^{2+}) through liquid phase ion exchange. The study confirmed that these modified zeolites were effective in removing dimethyldisulfide and thiophene from the gas stream, showing high efficiency. T. Yu *et al.* (2022) also demonstrated that the main problem with the use of zeolites is a decrease in their selectivity and sorption capacity at high sulphur concentrations in the treated stream. Contamination of zeolites with hydrocarbons or other substances can block the active centres, which significantly reduces their efficiency. To solve this problem, methods are being developed to regenerate zeolites and increase their resistance to contamination, such as the use of additional modifiers or combinations with other sorbents.

It is worth noting that the efficiency of zeolites in removing thiophenes and mercaptans depends not only on their structure but also on process conditions, such as temperature, pressure and composition of the

processed mixture. An important area of research is the development of modified zeolites with improved catalytic and sorption properties capable of handling high sulphur concentrations. The creation of technologies that minimise zeolite degradation and facilitate their regeneration are prioritised to ensure sustainable operation in industrial conditions. The use of activated carbons has confirmed their economic affordability and ease of integration into existing production processes (Kosogina *et al.*, 2019). However, their low efficiency in handling heavy hydrocarbons and the impossibility of multiple regenerations made them less suitable for deep sulphur removal tasks. This confirms the need to use activated carbons only in combination with other technologies or for temporary solutions.

S.Z. Naji & C.T. Tye (2022) investigated the use of activated carbon as a precursor and catalyst in biodiesel production. They concluded that activated carbon can be easily integrated into technological processes due to its availability and ease of use. This makes it an attractive option for improving refinery operations with minimal modification of existing equipment. K.L. Tan & K.Y. Foo (2022) determined that, despite their economic availability, activated carbons have several limitations in the treatment of refinery wastewater. Their adsorption capacity can decrease at high pollutant concentrations, requiring frequent regeneration or replacement of the material (Hulevskyi & Postol, 2022). In addition, activated carbons are less effective at removing more complex or high molecular weight organic compounds, which limits their use in more severe processing conditions.

X. Wang *et al.* (2021) confirmed the results of the study that activated carbons can be successfully integrated into existing processes without the need for significant technical changes. This underscores their attractiveness as a cost-effective solution that allows petrochemical plants to quickly adapt to the requirements of purification. At the same time, these carbons provide a sufficiently high level of adsorption for most common pollutants, which confirms their wide applicability in current technologies. Metal-organic frameworks, despite their high selectivity and flexibility in structure tuning, have demonstrated insufficient resistance to industrial conditions. The high cost of synthesis and the need to develop more stable structures are the main obstacles to their widespread use. Nevertheless, their potential in the long term is high, making them an attractive target for further research.

The study by J. Guo *et al.* (2021), which determined that metal-organic framework materials have several advantages, such as high selectivity in the sorption of various pollutants and the possibility of modifying their structure to improve properties, is noteworthy. This allows MOFs to effectively remove specific pollutants, such as sulphur compounds, even at low concentrations in the stream. In addition, the ability to modify structure parameters such as pore size and chemical environment

opens additional opportunities for their application in various fields, including petrochemicals. S.G. Yunusov *et al.* (2023) noted that desulphurisation of coke oven gasoline and diesel fraction blends by alternative methods (adsorption, extraction, oxidative desulphurisation using hydrogen peroxide and alkyl peroxides) is an important task to reduce sulphur emissions, cheapen refining, and improve fuel performance. For instance, the authors proposed to use adsorbents to prevent the loss of octane fuel. However, their proposed methods require further improvement to ensure stability and efficiency under industrial conditions. The results of Z. Zaidi *et al.* (2023) concur with the results of this study as they confirm the effectiveness of alternative desulphurisation methods in reducing the sulphur content of fuel fractions. The application of such methods as adsorption and catalysis can significantly improve the quality of coke oven petrol and diesel fraction blends, reducing their harmful impact on the environment.

Hybrid methods combining adsorption with catalytic desulphurisation showed the best results in terms of sulphur removal depth. In addition, the ability to regenerate adsorbents reduced operating costs. However, the complexity of their integration into the existing infrastructure and the high initial cost of the equipment limits their use in some cases. These aspects require further optimisation to ensure greater technological adaptability. S. Gooneh-Farahani & M. Anbia (2023) also conducted a study, the results of which confirmed that hybrid methods combining different approaches to remove sulphur from hydrocarbon streams show high efficiency in achieving deep purification. The use of technologies such as the combination of adsorption with catalytic process or membrane filters can increase the degree of sulphur removal with less energy and feedstock. These methods can significantly improve the quality of petrochemical products while meeting stringent environmental standards.

A. Asghar *et al.* (2022) determined that the introduction of hybrid technologies into biorefinery infrastructure faces several challenges, including the need to modernise existing equipment and the high cost of new systems. One solution may be to introduce hybrid technologies in a phased manner, allowing them to be gradually integrated into existing processes. Equally, an important step is to develop flexible and economically feasible schemes for the regeneration and replacement of the materials used, which will help to reduce initial costs and improve system longevity. Their study confirms that hybrid methods do provide significant improvements in the efficiency of sulphur removal from hydrocarbon streams. By combining different technologies, the limitations of each can be compensated for, providing deeper purification and lower operating costs. This confirms the potential of hybrid solutions as a key element in modernising refining processes to meet modern environmental requirements.

Comparison of the methods showed that the choice of technology depends on several factors, including sulphur concentration, hydrocarbon stream composition, economic viability and equipment availability. This demonstrates the need for an integrated approach when planning desulphurisation systems. Integration of several methods may prove to be the most effective strategy to meet both environmental and economic requirements. D.C.C. da Silva Medeiros *et al.* (2022) concluded that when selecting adsorption technology for the treatment of hydrocarbon streams, process efficiency, economics and the composition of the stream itself are key factors. Efficiency depends on the ability of the adsorbent to selectively remove pollutants with minimum energy and material consumption. It is also important to consider the composition of the hydrocarbon stream, as the presence of various impurities can significantly influence the choice of adsorbent and the optimisation of the treatment process.

T. Alomar *et al.* (2024) determined that to achieve both the environmental and economic goals of refineries, it is often necessary to combine several treatment methods. For instance, the use of adsorption in combination with catalytic processes or membrane technologies can increase the degree of pollutant removal and reduce the cost of material recovery. Thus, the integration of different technologies can achieve an optimal balance between costs and environmental requirements, which is critical for the sustainable operation of a refinery. Thus, the effectiveness of adsorption technologies directly depends on the composition of the hydrocarbon stream and the selected adsorbent. In the case of multi-component streams, a combination of different treatment methods can significantly improve the results compared to a single approach. This confirms the need for a more careful selection and combination of technologies to achieve optimal performance at minimum cost and compliance with environmental standards.

Conclusions

The results of the study identified the key features and limitations of various adsorption methods for removing sulphur from hydrocarbon streams, as well as their applicability in different refinery conditions. Zeolites have demonstrated high selectivity and efficiency for removing sulphur compounds such as thiophenes and mercaptans. However, their sensitivity to heavy hydrocarbon contamination and reduced performance at high sulphur content have limited their use in highly

contaminated streams. They remained the optimal solution for deep treatment of light hydrocarbon fractions. Activated carbons have proven to be the most cost-effective and affordable option for companies with limited financial resources. They are effective for the pre-treatment of low-sulphur hydrocarbon streams, but their limited regeneration capacity and reduced efficiency with heavy hydrocarbons reduce their attractiveness for more complex processing conditions. MOFs represent an innovative method with the highest selectivity and the ability to be customised to specific applications. However, their high cost and insufficient operational stability make them less competitive for widespread use in current industrial environments. Nevertheless, they remain a promising area for further research and technological improvements.

Hybrid methods that combine adsorption and catalytic desulphurisation have shown the highest efficiency for the deep treatment of complex hydrocarbon streams. At the same time, they are characterised by high implementation costs and complexity of integration into existing technological processes. Additional materials, such as carbon molecular sieves, metal oxides and sulphides, modified clays and bentonites, have demonstrated specific advantages, but their application depends on individual processing conditions. UMCs are versatile for optimising desulphurisation processes, making them an important element in the development of the refining industry in the face of environmental challenges. The choice of the optimal adsorption method is determined by the economic and technical capabilities of the refinery. Large refineries can effectively use hybrid technologies and MOFs, while smaller refineries can integrate activated carbons or modified clays to reduce costs. The main limitation of this study is the lack of experimental data in refinery conditions, which limits the ability to accurately assess the effectiveness of the methods. In the future, a detailed study of the long-term stability and regeneration of adsorbents such as metal-organic frameworks in real industrial conditions are required.

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Conflict of Interest

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Промислові адсорбційні методи зниження вмісту сірки у вуглеводневих потоках

Фазіл Рахімлі

Кандидат наук з нафтохімії
Азербайджанський державний університет нафти і промисловості
AZ1010, просп. Азадлика, 20, м. Баку, Азербайджан
<https://orcid.org/0009-0006-3970-308X>

Нігар Мамєдова

Доктор філософії, доцент
Азербайджанський державний університет нафти і промисловості
AZ1010, просп. Азадлика, 20, м. Баку, Азербайджан
<https://orcid.org/0000-0001-8508-8192>

Анотація. Досліджено промислові адсорбційні методи зниження вмісту сірки у вуглеводневих потоках з акцентом на їх технічну ефективність та технологічну адаптивність на нафтопереробних заводах. Проведено порівняльний аналіз використання цеолітів, активованого вугілля, металоорганічних каркасів, вуглецевих молекулярних сит, оксидів металів, полімерних матеріалів, сульфідів металів, модифікованих глин і бентоніту для зниження вмісту сірки у вуглеводневих потоках. Адсорбція з використанням цеолітів та металоорганічних каркасів виявилася високоефективною для видалення сірковмісних сполук, таких як тіофени та меркаптани, особливо при високих концентраціях сірки. Однак ці методи вимагають значних капітальних витрат і складної інфраструктури для масштабування. Активоване вугілля, незважаючи на його доступність та економічну ефективність, продемонструвало нижчу ефективність у видаленні сірки з важких вуглеводнів та обмежені можливості регенерації. Гібридні методи, що поєднують адсорбцію з каталітичною десульфурацією, виявилися перспективними для глибокого видалення сірки і зниження експлуатаційних витрат завдяки можливості регенерації адсорбенту. Для великих заводів оптимальними є гібридні технології та методи з використанням цеолітів і металоорганічних каркасів, що забезпечують високу ефективність при дотриманні екологічних стандартів. Для малих і середніх нафтопереробних заводів економічно доцільними є технології з використанням активованого вугілля. Таким чином, вибір методу адсорбції залежить від специфіки підприємства, типу потоку вуглеводнів та можливостей впровадження інноваційних технологій

Ключові слова: цеоліти; металоорганічні каркаси; каталітична десульфуризація; нафтопереробні заводи; активоване вугілля