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A comprehensive Review on Gasoline Adsorptive Desulfurization Using Activated Carbon

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Abstract

The need for clean transport fuels in the future prompted a study of advanced desulfurization technologies. Sulfur compounds in gasoline have a negative environmental impact, which contributes to acid rain formation, and from the point of view of human health, they cause respiratory and cardiovascular problems, including poisoning of engines and catalysts. The conventional method of hydrodesulphurization works perfectly, but it is usually carried out at high temperatures, it is not capable of removing refractory sulfur-containing species, thiophenes, and dibenzothiophenes, and it is too expensive. Adsorption desulfurization on activated carbon has emerged as a promising new approach due to its wide surface area, hierarchical porosity, and controllable surface chemistry. In this article, the latest developments in gasoline desulfurization using AC are reviewed with the latest Feed-stocks advances for AC, surface modification methods, and adsorbate interaction mechanisms. For example, date pits, are one of the source of activated carbon due to ecological and economic reasons. However, major problems still exist, such as poor adsorption capacity and the lack of regeneration and selectivity in the presence of various inhibitors. Future perspectives are aimed at the development of better adsorbent design, regenerability, and the implementation of AC-based ADS in a large scale." for AC-based ADS system design and deployment are projected as a feasible pathway to ultra-low-sulfur fuels.

Keywords: *Activated Carbon, Adsorptive Desulfurization (ADS), XRF, Gasoline, Sulfur Compound*

1. Introduction

The significant increase in demand for fossil fuel energy has resulted in severe environmental and health concerns, particularly owing to the combustion of sulfur-containing transportation fuels. The combustion of these fuels releases sulfur oxides (SOx), which are a major contributor to alevecid rain, air pollution, and various respiratory disease in humans [1].
To mitigate the environmental and health impacts of sulfur emissions, international and regional organizations have established stringent limits on the sulfur content in transportation fuels. Table 1 summarizes the maximum allowable sulfur content in transportation fuels across different countries and regulatory bodies.

Table 1: Comparative Global and Regional Sulfur Content Regulations in Transportation Fuels (2024–2025).

Country / Regulatory Body	Fuel Type	Maximum Sulfur Content (ppm)	Regulation Year	Reference
United States (EPA)	Gasoline	10 ppm (annual average)	Tier 3 standard, implemented since 2017; max 80 ppm per batch	[2]

Iraq (National Average)	Gasoline (domestic fuel)	Around 500 ppm has been reported in local studies.	-	[3]
European Union (EU)	Gasoline / Diesel	10 ppm	Euro V standard (Directive 2009/30/EC) applies to all road fuels	[4]
China (National VI)	Gasoline / Diesel	10 ppm	China VI was implemented in 2019, equivalent to Euro 6	[7]
India (BS VI Standard)	Gasoline / Diesel	10 ppm	Nationwide since April 2020	[5]
Brazil	Gasoline / Diesel	50–1800 ppm	Regional variation; ongoing transition to low-sulfur fuels	[6]
Argentina	Diesel	~2500 ppm	Limited ULSD adoption; gradual reduction underway	[5]
Peru	Diesel	up to 5000 ppm	Developing-stage sulfur control policies	[8]
UNEP Global Average	—	10 ppm (developed), > 1000 ppm (developing)	Reflects global disparity in fuel standards	[9, 6]

- The values for the United States, the European Union, India, and China show the official regulatory limits set by national gasoline quality standards (Tier 3, Euro V/VI, BS VI).
- Data from Brazil, Argentina, and Peru show that transitional sulfur concentrations change from place to place because of refinery modernization and the rate at which low-sulfur fuel is used.
- UNEP's global numbers show average sulfur levels, which show the difference between wealthy countries (≤ 10 ppm) and underdeveloped countries (> 1000 ppm).
- The mass fraction of sulfur in gasoline is measured in parts per million (ppm). Ten ppm is around 0.001 wt%.

Traditional desulfurization processes, such as hydrodesulphurization, have proven efficient in lowering sulfur levels. However, hydrodesulphurization often requires high temperatures and pressures, and it consumes considerable amounts of hydrogen. Moreover, it may not be fully effective at eliminating sulfur from fuels, especially refractory sulfur compounds such as thiophene and its derivatives, which constitute a substantial fraction of the sulfur present in fuels [9]. Furthermore, hydrodesulphurization may reduce the octane rating of gasoline due to olefin saturation, thereby limiting its application in substantial desulfurization processes [10].

Considering environmental regulations and the demand for cleaner fuels, alternative desulfurization approaches are being developed. Adsorption desulfurization (ADS) is consider one of the most promising alternative desulfurization technologies. ADS functions at gentler temperatures and is particularly selective for sulfur compounds. Its porosity and altered surface chemistry enable it to bring sulfur content down to very low levels [10]. AC is a well-known candidate for ADSP applications in gasoline desulfurization. Activated carbon has a high capacity and selectivity for sulfur-containing compounds, especially refractory organic sulfur compounds like dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) [11]. The adsorption capacity of modified activated carbon was much larger than that of commercial activated carbon (2–6 times depending on the modification) [11].

This study highlights advances in gasoline desulfurization with activated carbon, covering fundamental concepts, material properties, modification strategies, and future possibilities.

2. Activated carbon

Activated Carbon is a type of Carbon which has high porosity and large surface area, therefore, it has high versatility as an adsorbent. therefore, it is an ideal adsorbent for various desulfurization applications. The carbon can be prepared from different raw materials and this results in varying properties in the final product. Commonly used raw materials for activated carbon production include coal, coconut shells, polyurethane plastic waste, coke and other biomass including date pits, rice husks, and cows dung[10,13]. The therefore regular selections of the raw materials influence the properties of the material such as the pore structure, surface chemistry and effectiveness of the activated carbon therefore can be tailored to different applications.

Activated carbon is composed of carbon atoms and that are arranged in a random structure or disorderly manner. The process of activation removes non-carbonaceous or volatile materials from the carbon and this results in the formation of microspores, mesoporous, and macrospores. These pores serve as adsorption sites where they can be attracted by target molecules and bind to the inner surface of the carbon[14]. Activated carbon has distinctive physical and chemical properties. Its distinguishing feature is the extremely high porosity, and hence the internal surface area, which may exceed one thousand square meters per gram. This large surface area and large number of porous sites enable it to absorb a wide spectrum of compounds from both gas and liquid phases[14,15], and the table 2 shows a systematic comparison between the experimental results obtained from the recent studies (2020-2026) on Adsorptive Desulfurization (ADS) with different types of Activated Carbon (AC). This summary is intended to explain the connection between the physical characteristics of the adsorbents (such as surface area, pore volume, etc.) and the adsorbents' ability to perform (adsorption capacity) at specific operating conditions. Applications of activated carbon are numerous minor to its great absorption capabilities or features. These applications include water purification, gas mask filters, decolorization of sugar, and controlling odor. Moreover, activated carbon can also be used as a catalyst support. In the recent past, activated carbon has gained wide application in the desulfurization of petroleum fractions due to its high surface area, adjustable pore structure and surface chemistry. This process involves the efficient adsorption of sulfur-containing compounds such as thiophenes, benzothiophenes, and dibenzothiophenes from gasoline, diesel and kerosene fractions[13]. Activated carbon can also be used as a catalyst support, if impregnated with catalytic material. and hence the activated carbon supports the process as a catalyst. This creates high flexibility wherein high desulfurization rates of over 90% are obtained in the case of activated carbon of coconut shells, polymers, and agricultural byproducts, under optimal conditions[17]. In contrast to hydrodesulfurization, adsorption by activated carbon presents advantages in terms of operation simplicity, lower energy consumption, and the absence of hydrogen [12]. Moreover, activated carbon-based systems are highly flexible, allowing surface modification, such as metal impregnation or the incorporation of acidic/basic groups for increased selectivity of recalcitrant sulfur compounds. In conclusion, activated carbon is a suitable material for the deep desulfurization of petroleum distillation fractions to meet the requirements of ultra-low sulfur fuels under stringent environmental regulations [18,16].

Table 2: A comparative study of recent research (2020-26) on adsorptive desulfurization using activated carbon.

Adsorbent Type	**Precursor**	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Adsorption Capacity (mg/g)**	**Target Compound**	**Operating Conditions**	**Reference**
Modified AC (H3PO4/HNO3)	Waste Tires	926.44	0.51	254.45	DBT	Room Temp, Model Fuel	[14]
Biochar	Eucalyptus Waste	2592.2	-	172.5	DBT	High SSA focus	[15]
AC (KOH activation)	Pinecone	-	-	High	DBT	Extended activation time	[16]
AC	Date Seed + PET	672.22	-	-	DBT	3.16 nm pore size	[17]
Modified AC (Oxidative/Metal)	Coconut Shell	-	-	+59% vs Raw	DBT	Synergistic modification	[18]
Acidic AC	Corncobs	Low	-	-	DBT	1.38 nm pore size	[19]
Renewable AC	Food Waste	-	-	6.3 (S)	DBT	Model Jet/Diesel	[20]
Nanoporous AC	-	-	-	-	DBT/4,6-DMDBT	Solvent role study	[21]
Various ACs	Biomass	-	-	-	Sulfur	Economic comparison	[9]

- Overall, it can be inferred that the specific surface area of biochar (SSA), such as 2592.2 m2/g in case of eucalyptus derived biochar, typically has a positive correlation with the capacity of the biochar for adsorptive capacity, but the surface chemistry (functional groups) is also of critical importance
- As shown by Tsai et al. 2025[14] and Neves et al. 2024[18], the performance of raw activated carbon can be greatly improved by chemical modification (e.g., impregnation with H3PO4, HNO3, and/or metal ions).
- Feedstocks Diversity: There is an increasing interest in the application of sustainable and low-cost Feedstocks that are derived from waste tires, agricultural residues (corncobs, pinecones, date seeds), and food waste, which is consistent with green chemistry principles.
- Operating Conditions: Most studies have been conducted under room temperature and at atmospheric pressure conditions for ADS, which is quite energy efficient as compared to conventional hydrodesulfurisation (HDS).

3. Raw Materials for Activated Carbon Production

Choice of raw materials has a significant effect on the structural characteristics of the activated carbons and, consequently, on their total adsorption capacity and application. Different carbonaceous precursors can be used, each one having its own advantages and disadvantages for the production of activated carbon. In the literature, a wide range of materials has been successfully utilized, including various types of coal, different wood species, and agricultural and industrial residues [19-21].

3.1 **Coal-Based Activated Carbon:** Anthracite, bituminous, and lignite coal constitute the most common and traditional precursors for the production of activated carbon. Coal-based ACs often exhibit a primarily microporous-mesoporous structure, which gives them outstanding performance for gas-phase activities such as the elimination of volatile organic compounds and tiny gas molecules[24]. The increased carbon content and comparatively low volatile matter in anthracites render them especially appropriate for the production of activated carbons with superior mechanical strength and thermal stability. The environmental consequences of coal mining and its non-renewable characteristics are factors prompting research into alternative precursors.[22].

3.2 **Wood-Based Activated Carbon:** Wood, harvested from multiple types of trees, is also a key raw material. Wood based activated carbons are generally of more mesoporous structure than coal based. The wider pore size distribution makes them particularly effective in the removal of larger organic molecules as would be the case of decolourization in liquid phase or having applications at industrial effluent[25].The sustainability of wood as part of renewable resources and the potential to utilize wood waste products, it is an attractive candidate for activated carbon production[25].

3.3 **Agricultural By-products and Biomass:** In the last few years, it has gained much interest to use agricultural by-products and different types of biomass as a sustainable and low-cost precursor for activated carbon. Available studies are increasingly carried out with materials such as coconut shells, pecan shells, rice husks, date-palm leaflets[19-21].Coconut shells are valued for the ability to render activated carbons with a high content of micropores and narrow micropore size distributions. As a result, such expandable materials are also highly responsive for water filtering, especially for removal of trace organic pollutants and chlorine in addition to situations requiring high capability to adsorb some contaminants. Here, the utilization of an abundant and waste material provides us with a self-sustained AC supply, helps with waste management and environmental considerations that make it an attractive substitute for expensive traditional methods[26].

3.4 **Influence of Raw Material Properties:** The intrinsic characteristics of those precursors such as carbon, volatile matter, ash and lignin/cellulose composition of them determine the suitable activation conditions and have great influence on final pore structure property, surface chemistry as well[27]. For instance, Materials with higher lignin contents may produce activated carbon which has a greater mass fraction of micropores than materials with higher cellulose content. Deciding on the precise raw materials is a strategic choice, based upon what application you intend putting it to and the necessary adsorptive properties of the activated carbon.

4. Modification Techniques

Although activated carbon in its original state exhibits superior adsorption properties, its surface characteristics can be further optimized and improved through diverse modification methods. These modifications seek to introduce specific functional groups, modify pore architectures, or integrate additional materials to enhance selectivity, adsorption capacity, and regeneration efficiency for specific applications[25,26].

4.1 **Physical modification:** The main aim of physical modification is to alter the structure of the pore and its specific surface area of activated carbon without substantially changing the chemical composition.

- **Thermal Treatment:** Thermal processing of AC at different high temperatures results in the redistribution of pore sizes and changes in surface morphology. As an example, the high temperature treatment can strip away some surface functional groups, and thus, enhance the hydrophobicity of the carbon surface[30].
- **Physical Additives:** In this case, the activated carbon matrix is impregnated with the materials which include metal oxides, nanoparticles or polymers. These additives are designed to either improve the catalytic capacity or introduce antibacterial functionality or greater selectivity to a certain pollutant[29].

4.2 **Chemical Modification**: The most common method of modification of the surface chemistry of activated carbon is one that introduces a specific functional group.

- **Oxidation:** This process uses strong oxidants (e.g., nitric acid, hydrogen peroxide, or ozone), to introduce oxygen-containing functional groups, such as carboxyl, hydroxyl, and carbonyl groups. Oxidation raises the surface acidity which greatly increases the affinity of the carbon to the basic pollutants and heavy metal ions[31].
- **Reduction:** On the other hand, reduction treatments seek to reduce the surface acidity and increase the basicity, adjusting the carbon to different adsorption targets.
- **Nitrogen Doping**: This is a process in which nitrogen-containing functional groups (e.g., amines, amides) are introduced to activated carbon usually by treating the carbon with nitrogen-containing organic or inorganic compounds at elevated temperatures. Doping with nitrogen increases the adsorption capacity of the material towards CO2 and heavy metals, as well as improves the catalytic properties of the material[32].

4.3 **Biological Modification**: is a new, eco-friendly method involving the use of microorganisms or enzymes to modify the AC surface.

- **Microbial Colonization:** BAC is produced using activated carbon as a support surface to allow the growth of microorganisms. The degraded adsorbed organic pollutants are degraded by the immobilized microorganisms and this further increases the operational lifespan of the activated carbon itself[33].
- **Enzymatic Modification:** In this, the specific enzymes are immobilized on the carbon surface to catalyze the targeted biochemical reactions to increase the efficiency of bioremediation of complex pollutants[34].

4.4 Impacts of Modification: The choice of the modification technique depends on the intended use. Basic-functionalized ACs reportedly provide higher performance in the adsorption of acidic gases, whereas acidic-functionalized ACs are more suitable to capture basic pollutants. Its activity for catalysis or photo catalysis Abatement can significantly improve by using specific metal nanoparticles. Hence, activated carbon has been used with the nanoparticle to produce a highly efficient catalyst and/or photo catalyst. The surface modification techniques strongly promote the activated carbon properties, thus, extending the application and efficiency in several environmental, industrial as well as medicinal applications[27,24,22].

5. Efficacy and Economic Feasibility for Desulfurization

Choice of appropriate precursor is an important economic issue in adsorptive desulfurization. The cost of AC is largely influenced by the sourcing availability impact and processing needs for raw materials [35]. While reliable evaluation of performance parameters like adsorption capacity and selectivity is important, the industrial scalability primarily relies on relatively cheaper and renewable Feedstocks [29,30]. It has been reported that low-cost adsorbents with good capacity taken for inorganic and organic contaminants can be prepared through different wastes and biomass, such as tea waste, maize cobs etc. at lower cost[30,31] .An important aspect of economic viability is a detailed LCC analysis of everything from feedstocks supply to activation technique, in order to assess the comparative merits of different production routes [39]. A comparative economic study of some AC predecessors will be described. The Table 3 below summarizes the key information for ease of comparison along with their desulfurization efficiency and raw material cost for making a selection on the most potential candidates to use industrially.

Table 3: Comparative Evaluation of Raw Materials Based on Desulfurization Efficiency and Economic Feasibility.

Raw Material	Removal Efficiency (%) (Sulfur Compounds)	Maximum Capacity (mg S/g)	Optimal Modification Method	Economic Cost (Assessment)	References
Bituminous Coal / Anthracite	70–90% (DBT & other sulfur compounds)	15–30	Chemical activation with KOH / H_3PO_4	Relatively High	[40]
Coconut Shells	up to 98% (Dibenzothiophene)	25–45	Steam activation / H_3PO_4 activation	Low to Medium	[41]
Date Pits	~95% (DBT)	~23.8	Chemical activation with $ZnCl_2$	Very Low (agro-waste)	[42]
Wood Biomass	75–88% (DBT)	15–28	Chemical activation with H_3PO_4	Medium	[36]
Coal (general)	70–85% (various sulfur compounds)	10–20	Acid washing + activation	Low (raw coal cost)	[43]
Modified Clay-Based Adsorbents (Bentonite, Montmorillonite, Kaolinite + Carbon Composite)	65–80% (DBT)	8–18	Carbon impregnation, acid activation, polymer coating	Very Low	[9]
Plastic Waste / Waste Tires (Pyrolyzed Carbon Materials)	80–95% (DBT)	20–120 (typical), up to ~250 under ideal conditions	Pyrolysis + H_3PO_4/HNO_3 modification	Variable	[14]

- Efficiency and Cost: A general opposite relationship exists between cost and efficiency. Materials derived from agricultural or waste sources (e.g., date pits, coconut shells, plastic waste) provide exceptional performance at a low raw material cost, rendering them the most economically viable and environmentally sustainable option.
- The maximum capacity of a material is closely correlated with its surface area and pore size distribution. Materials characterized by high microporosity, such as coconut shell carbon, are highly effective in adsorbing thiophenic chemicals.
- The modification procedure is essential for transforming a raw material into an effective product. Chemical activation (utilizing KOH, H_3PO_4, $ZnCl_2$) is the predominant method for generating specific porosity designed for sulfur compounds.

- Recommendation: The data in the table 3 suggests that carbon obtained from coconut shells and date pits is an excellent selection for achieving high efficiency, maximum capacity, and minimal economic cost, particularly in areas where these materials are readily accessible.

6. Adsorptive desulfurization (ADS) principles

Desulfurization and adsorption are mass transfer processes in which sulfur molecules from the liquid phase adhere to the surface of a solid [9] as illustrated in Figure 1. This method is preferred because of its simplicity and low energy consumption. Adsorptive desulfurization (ADS) is a hydrogen-free process that removes sulfur-containing compounds from liquid fuels using solid adsorbents [43]. Sulfur content is commonly measured using X-ray fluorescence spectroscopy (XRF) (NEX QC, Rigaku. Corporation, Japan). The adsorption process is categorized into equilibrium adsorption and non-equilibrium adsorption.

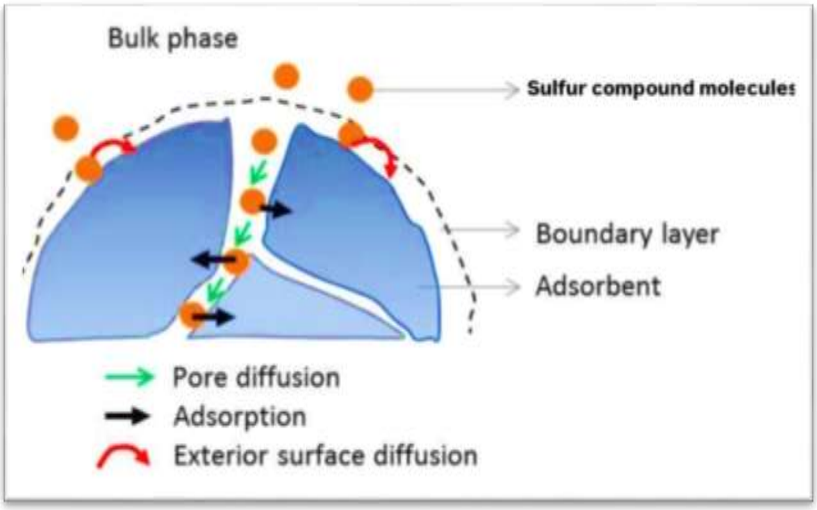

Fig.1. The adsorption process illustrating mass transfer and diffusion mechanisms within adsorbent particles.

Fixed beds operate with an unsteady state operational mode. The prediction of required adsorbent quantity for fixed bed operation needs complete testing which demands substantial computational efforts.
Equilibrium, kinetic, thermal, and hydrodynamic considerations, along with physical data, are required for the design of the adsorptive desulfurization process [44] as illustrated in Figure 2.

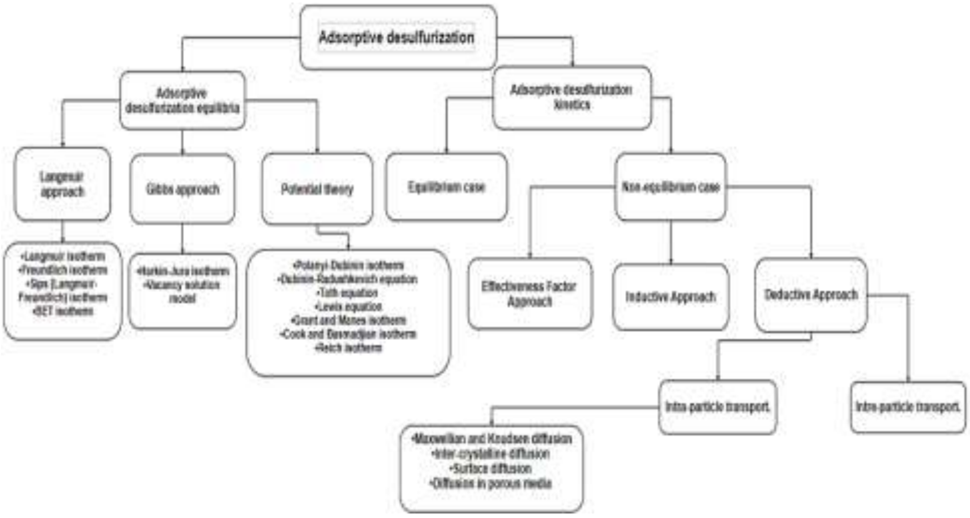

Fig. 2. Conceptual Framework of Adsorptive Desulfurization Equilibria and Kinetics

6.1 Adsorptive desulfurization equilibria

When a liquid is exposed to the adsorbent, the solid adsorbs a certain amount of the fluid. The amount adsorbed when equilibrium is established is a function of the final concentration C and temperature, and is given by:

$$q^* = f(C.T_g) \tag{1}$$

At a fixed temperature, q* is only a function of C, which is called an adsorption equilibrium isotherm.

$$q^* = f(C) \tag{2}$$

There are numerous isotherm models used to interpret each type of isotherm. They are based on three different approaches as follows[45].

6.1.1 Langmuir approach

This approach, given by Langmuir in 1918, is originally a kinetic one, assuming the adsorption system in dynamic equilibrium, where the rate of evaporation is equal to the rate of condensation. The Langmuir isotherm remains the most useful for data correlation in separation processes[45]. The following isotherms are based on the Langmuir approach:

- Langmuir isotherm
- Freundlich isotherm
- Sips (Langmuir- Freundlich) isotherm
- BET isotherm

Table 4 presents a summary of prevalent adsorption models and their fundamental characteristics.

Table 4: Summary of Common Adsorption Isotherm Models and Their Characteristics

Isotherm Model	Equation	Description	References
Langmuir Isotherm	$\mathrm{qe} = \dfrac{\mathrm{qma\ \ KL\ Ce}}{1 + \mathrm{KL\ Ce}}$	Based on monolayer adsorption on a homogeneous surface, it assumes all sites are identical and no interactions between adsorbed molecules.	[46]
Freundlich Isotherm	$\mathrm{qe} = \mathrm{Kf\ Ce}^{\frac{1}{n}}$	Empirical model for heterogeneous surfaces; adsorption capacity increases with concentration; no saturation limit.	[45]
Sips (Langmuir–Freundlich) Isotherm	$\mathrm{qe} = \dfrac{\mathrm{Ks\ Ce}^{\beta s}}{1 + \mathrm{asCe}^{\beta s}}$	Combines Langmuir and the Freundlich models; it behaves like Freundlich at low concentrations and Langmuir at high concentrations.	[47]
BET (Brunauer–Emmett–Teller) Isotherm	$\mathrm{qe} = \dfrac{\mathrm{qs\ CBET\ Ce}}{(\mathrm{Cs} - \mathrm{Ce})\big(1 + (\mathrm{CBET} - 1)(\ \mathrm{Ce\ Cs}\ )\big)}$	Extends Langmuir theory to multilayer adsorption; widely used for surface area determination (e.g., N_2 adsorption).	[41]

6.1.2 Gibbs approach

Willard Gibbs, in his thorough examination of thermodynamics at equilibrium, posited that the adsorbent acts as a thermodynamically inert phase, whereas the adsorbate is mobile and not confined to specific surface locations. The Gibbs thermodynamic method, initially formulated for gas–solid systems, has been effectively adapted to characterize adsorption from liquid phases[49]. The following isotherms are based on the Gibbs approach:

- Harkin-Jura isotherm
- Vacancy solution model

6.1.3 Potential theory

The adsorption process, initially articulated by Polanyi in 1914, can be understood as the gradual accumulation of adsorbate molecules at the solid surface influenced by a potential field. The potential theory, initially formulated for gas–solid systems, has been effectively adapted to characterize adsorption from liquid phases, wherein the adsorption potential is associated with the equilibrium concentration of the solute instead of vapor pressure[50]. The following isotherms are based on the potential theory approach, as shown in Table 5:

- Polanyi-Dubinin isotherm
- Dubinin-Radushkevich equation
- Toth equation
- Lewis equation
- Grant and Manes isotherm
- Cook and Basmadjian isotherm
- Reich isotherm

Table 5: Recent Developments in Potential-Theory-Based Adsorption Isotherm Models.

Isotherm Model	Equation	Description / Notes	References
Polanyi–Dubinin Isotherm	$\mathrm{w} = \mathrm{w}^0 \exp\left[-\left(\dfrac{\mathrm{A}}{\mathrm{E}}\right)^2\right]$	Based on potential theory, the adsorption volume depends exponentially on the adsorption potential (A).	[51]

Dubinin–Radushkevich (D–R) Equation	$q_e = q_{max} \exp[-K_{DR}(\varepsilon)^2]$ where $\varepsilon = RT \ln(1 + 1/C_e)$	Describes micropore filling; used for physical adsorption with a Gaussian energy distribution.	[52]
Toth Equation	$q_e = \dfrac{(q_{max} K_T C_e)}{(1 + (K_T C_e)^t)^{\frac{1}{t}}}$	Semi-empirical model for heterogeneous surfaces; reduces to Langmuir when t = 1.	[51]
Lewis Equation	$q_e = \dfrac{(q_{max}\, b\, C_e)}{(1 + b\, C_e + c\, C_e{}^2)}$	Modified Langmuir form accounting for multilayer adsorption or molecule interactions.	[45]
Grant and Manes Isotherm	$\ln\left(\dfrac{C_e}{C_s}\right) = -K_G\left(\dfrac{V}{V_m}\right)^n$	Derived from potential theory; relates solute concentration to volume adsorbed.	[45]
Cook and Basmadjian Isotherm	$q_e = q_{max}\left[1 - \exp(-\alpha\, C_e{}^{\beta})\right]$	Empirical model fitting wide adsorption data, based on energy distribution.	[53]
Reich Isotherm	$q_e = \dfrac{\left(q_{max}\, (K_R C_e)^{\frac{1}{n}}\right)}{\left(1 + (K_R C_e)^{\frac{1}{n}}\right)}$	Similar to the Sips model, it accounts for surface heterogeneity in potential field theory.	[51]

6.2 Adsorptive desulfurization kinetics

Fundamental to the design of any adsorption equipment is an understanding of what goes on in a fixed bed. The problem has received increasing attention over the last forty years, with many solutions being offered for different operating conditions. The failure, in general, of those solutions to predict the behavior of large beds with accuracy is a measure of the complexity of the phenomena being analyzed.

It is clear that better design waits on a more thorough understanding of the molecular processes involved, and an appreciation of their relevance to a mathematical description of the system. However, several investigators have studied the problem, and the solutions that have been obtained can be broadly classified into two general types: the equilibrium and the non-equilibrium theories[47,48].

The pseudo-first-order (PFO) model is applied by plotting the plot of ln(qe-qt) against t and the amount of sulfur that can be adsorbed at equilibrium (qe) and rate constant (K1) are estimated from Equation (3) as shown in the plot of ln(qe-qt) against t, in Figure (3) where the amount of sulfur compounds adsorbed at time t (qt)[55].

$$\ln(qe - qt) = (\ln qe - K1\, t) \tag{3}$$

The plot of t/q versus t, for the pseudo second order rate (PSO) model Equation (4) is presented in Figure (4)[55].

$$\frac{t}{qt} = \frac{1}{K2qe2} + \left(\frac{1}{qe}\right) t \tag{4}$$

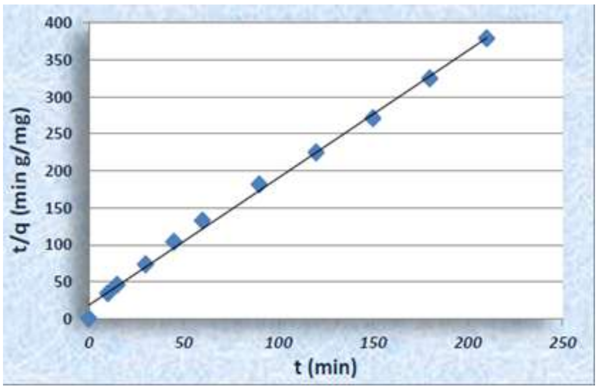

Fig. 3. Pseudo-First Order Model

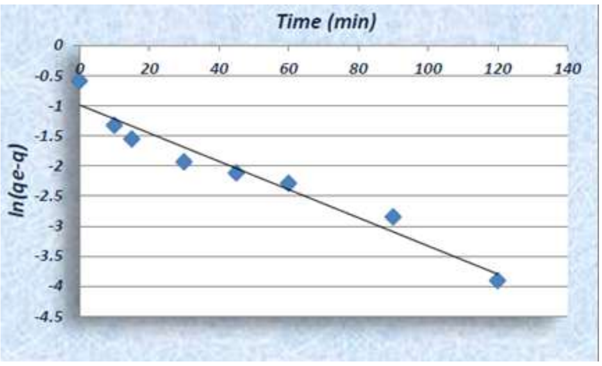

Fig. 4. Pseudo-Second Order Model

6.2.1 Equilibrium case

When resistance to the transfer of sorbate from the fluid to the adsorbed state is negligible, concentrations in the bulk fluid and in the solid at a point in the bed are related through the adsorption equilibrium isotherm[54].

Equilibrium is achieved when the surface of a clean, non-porous adsorbent comes into contact with an adsorbed gas, and the gas flows freely through the liquid contact layer near the surface. The adsorption process occurs extremely rapidly, and the term "self-rate" is used to describe this characteristic speed of the reaction[56].

Physical adsorption at a surface is virtually instantaneous, so that the rate of adsorption in a microporous adsorbent is almost invariably controlled by diffusional resistance to mass transfer rather than by the intrinsic surface kinetics[57].

6.2.2 Non-equilibrium case

In non-equilibrium conditions, concentration gradients develop across the boundary film outside the granule and through the granule itself[58].

There is a formidable body of literature dealing with the solution of fixed-bed equations for non-equilibrium operation. Two general approaches can be discerned. The first is a deductive approach; the relevant mechanisms of transfer are picked out and combined to give a rate equation[59]. The second is inductive in the sense that a solution is used that has been found for a specific kind of rate expression. The actual conditions of operation for which the solution is required are then arranged in the form of this rate expression.

Table 6: Summary of Kinetic Modeling Approaches in Adsorption Processes.

Approach	Description	Key Concepts / Equations	References
Deductive Approach	Identifies physical transport mechanisms and combines them into rate equations.	Inter-particle & Intra-particle transport. N = kf (Cf – Cs) Diffusion types: Maxwellian, Knudsen, Surface, Porous.	[53,54]
Inductive Approach	Simplifies the model by removing detailed internal mass and heat balances.	Linear Driving Force (LDF): $\frac{dq}{dt} = kG\,(q* - q)$ Quadratic Driving Force (QDF): $\frac{dq}{dt} = \left(De\frac{\pi^2}{r^2}\right)(q* - q)$	[55,56]
Effectiveness Factor Approach	Considers internal and external diffusion resistance to evaluate real adsorption rates.	$\eta = \frac{(\text{reaction rate at surface})}{(\text{observed rate with diffusion})}$ (Driessen et al., 2022).	[64]

7. Factors of Desulfurization Efficiency

The efficacy of gasoline desulfurization by activated carbon is affected by various interconnected elements, including the characteristics of the adsorbent, operational parameters, and the composition of the fuel. A comprehensive comprehension of these elements is essential for optimizing the process and improving its economic feasibility.

7.1 Physical and Chemical Characteristics of Activated Carbon

7.1.1 **Surface Area and Pore Volume:** The whole face is found the main site for adsorption. A greater value of specific surface area will naturally give better adsorption. However, the spatial distribution of pore sizes is an equally important factor. Among them, micropores (< 2 nm) are favorable for the adsorption of small thiophene molecules such as dibenzothiophene (DBT), while mesopores (2-50 nm) help larger molecules access to interior pore structure [63,64].

7.1.2 **Surface Chemistry**: Adsorption is determined by the physical (physisorption) and chemical (chemisorption) factors. The presence of functional groups on the activated carbon surface, including carboxyl, hydroxyl and lactone groups has a significant influence upon the selectivity and efficiency of sulfur removal. Basic groups like nitrogen-groups often enhance adsorption capacity through acid-base mechanism with the sulfur specie[65,66].

7.1.3 Adsorbate – Adsorbent Interaction Mechanisms

In addition to the pore filling effect, specific adsorbate–adsorbent interactions are responsible for the adsorption of thiophenic sulfur compounds onto activated carbon. The aromatic sulfur compounds, thiophene, BT, and DBT, have delocalized π-electrons which are able to interact with the graphitic basal planes of the activated carbon material via π–π interaction. The stronger between the two the more aromatic the sulfur compound and the higher the degree of graphitization of the carbon surface[13, 21].

Moreover, selectivity of adsorption is greatly influenced by acid – base interactions. The electron density of the carbon surface is modified by the presence of oxygen-containing acidic functional groups (e.g., carboxyl groups, phenolic groups) and nitrogen-containing basic groups (e.g., pyridinic-N, pyrrolic-N) that affect the affinity to Sulfur compounds[31,32]. Nitrogen doped activated carbons may also serve as electron donors and act to increase the amount of adsorption of electron deficient sulfur containing aromatics by Lewis acid – base interactions and π-complexation mechanisms[13,18].

Furthermore, the adsorption of sulfur under the presence of transition metals like Cu^+, Ag^+ or Ce can occur by direct coordination of S with transition metals and π-complexation. In this mechanism, electron donation from the sulfur aromatic ring to the vacant d-orbitals of the metal is concurrent with the donation of electrons from the metal to the π-electrons of the aromatic ring, resulting in greater and more selective adsorption of refractory sulfur compounds like DBT and 4,6-DMDBT[18,68]. These interactions could be reduced by competitive adsorption of aromatic hydrocarbons which can bind to the same π-electrons on the carbon surface[21,69].

7.2 Operational Parameters

7.2.1 **Temperature:** The relationship between temperature and adsorption capacity is complex. While higher temperature improves adsorption kinetics and allows for faster molecular transfer that would bring the system closer toward equilibrium, physisorption is typically exothermic. Hence, the excessively high temperatures could result in decrease of adsorption equilibrium capacity. An optimum temperature is commonly found which compromises of speed and volume[70].

7.2.2 **Contact Time:** Sufficient contact time of gasoline with activated carbon is important for sulfur molecules in the liquid to be distributed into adsorption sites in the pore walls. Lack of time prevents the system from reaching equilibrium, and so reduces efficiency. The longer the time, the greater the operating time and lower production, with little additional benefit after saturation point[71].

7.2.3 **Fuel/Adsorbent Ratio**: This is an expression that indicates the load on the adsorbent. A low ratio (i.e., high adsorbent dose) provides more efficient use of adsorption sites and removal efficiency, though the operation cost increases. In high ratio (small amount of adsorbent) the material sets more stress and it degrades quickly. The perfect combination is achieved when efficiency & cost are at a balance [71].

7.3 Characteristics of Feedstocks and Sulfur Compounds

7.3.1 **Initial Sulfur Concentration:** An elevated sulfur concentration in gasoline enhances the diffusion gradient, hence augmenting the initial adsorption rate. Nevertheless, it results in accelerated depletion of the adsorbent and rapid saturation, necessitating more frequent regeneration cycles[71].

7.3.2 **Classification of Sulfur Compounds:** The stripping of the sulfur compounds is highly variable. Simple chemicals, such as but not limited to hydrogen sulfide and mercaptans can be removed with reasonable ease. In contrast, thiophene (Th), dibenzothiophene (DBT), and especially their alkylated compounds (e.g., 4,6-DMDBT) are refractory due to their aromatic nature and steric hindrance, forcing the need for modified adsorbents or harsher operation conditions. [34,69].

7.3.3 **Modification with Active Metals**: Impregnating the activated carbon surface with metals such as copper (Cu), cerium (Ce), or silver (Ag) is one of the most efficacious ways for performance enhancement. These metals facilitate oxidation processes that transform refractory thiophenic chemicals into more polar and easily adsorbed sulfones, significantly enhancing process selectivity and efficiency [68].

7.4 **Presence of Competing Compounds (Competitive Adsorption):** Aromatic hydrocarbons (e.g., toluene, xylene) and other constituents in gasoline can compete with sulfur compounds for identical adsorption sites on the activated carbon surface. This competition significantly diminishes desulfurization performance, especially for unchanged carbons dependent on physisorption. Selective modification of carbons can alleviate this issue [69].

7.5 **Adsorbate concentration effects.** In gasoline desulfurization, the concentration of sulfur compounds (e.g., thiophene, benzothiophene) is often low, often in the parts per million (ppm) range. With such highly diluted conditions, the overall fluid velocity in the Mass Transfer Zone (MTZ) is not too sensitive, and simplified models of purification can be used **.**

The fluid density and velocity profiles across the MTZ can However, vary depending on the level of sulfur concentration or due to competitive adsorption by competing hydrocarbons that co-exist[72].

7.6 **Back mixing effects** in the case of high-velocity industrial processes that depend on pure plug flow, the axial dispersion term can be neglected, which in turn is common in high-velocity industrial operations. In case the axial dispersion is large, the model of the system is the axially dispersed plug flow. To ensure high desulfurization efficiency, radial dispersion is generally kept to a minimum through proper bed design and is typically not included in standard adsorption flow models[73].

7.7 **Thermal effects** The adsorption of sulfur compounds on activated carbon is an exothermic reaction. Although most designs assume an isothermal column, especially when the concentration of sulfur and the heat of adsorption are small, real-world adiabatic columns can experience an increase in temperature. The major heat effects may change the adsorption capacity and kinetics that necessitates the use of energy balances versus mass balance equations to accurately predict the temperature and concentration profile within the bed[74].

7.8 **Rate of adsorption effects.** The conditions of instantaneous equilibrium during the adsorption layer is seldom true in gasoline desulfurization because of mass transfer resistance. These resistances need to be included in effective models, and often reduced to a single-resistance expression using a mass transfer coefficient based on either an external liquid film or internal particle diffusion.

These resistances need to be included in effective models, and often reduced to a single-resistance expression using a mass transfer coefficient based on either an external liquid film or internal particle diffusion[75].

7.9 Adsorption equilibria effects

The stability and mobility of the MTZ is dependent upon the shape of the adsorption isotherm (usually Type I of sulfur on AC). When favorable isotherms are present, sharp boundaries form in the MTZ, and eventually stabilize in a steady-state pattern as the bed saturates. Conversely, when the isotherms are unfavorable or competitive adsorption occurs by the gasoline components, then the MTZ can expand and exhibit dispersive behaviour, resulting in premature sulfur breakthrough and decreased removal efficiency [41].

2. Challenges and future directions

Despite the great potential of activated carbon (AC) in gasoline desulfurization, numerous problems must be resolved to enhance the efficiency and scalability of this approach.

2.1 **Constrained Adsorption Capacity:** There are only limited active sites on the activated carbon for adsorption of sulfur compounds. Despite being modified by impregnation of basic substances or transition metal oxides to increase adsorption capacity; somewhat increased cost was included in these methods. In addition, the use of date pits for production of AC is problematic due to the variation in raw material quality. The differences depend on factors such as date variety and region of production. In addition, improving activation for optimal performance without increasing the cost is a major spot that deserves attention to in future. Further work should focus on improving the scalability of this approach, investigating other more efficient methods for activation, and assessing its long-term stability in practical applications[1,83].

2.2 **Regeneration Concerns:** In addition to disposing of the process waste, there remains a problem of reusing spent activated carbon. Ultimately, the adsorption sites of activated carbon achieve saturation and makes it harder for sulfur compounds to be desorbed. Regeneration processes may require high temperatures or harsh chemical reagents, which will possibly damage materials and reduce the long-term efficiency. Creation of more efficient and sustainable regeneration process or the improvement of activated carbon sources strengthening some means strengthens for practical such as gasoline desulfurization[1].

2.3 **Selectivity for Sulfur Compounds:** Despite AC's particularly for sulfur-based compounds), and other impurities in gasoline could impact the adsorption. Aromatic and nitrogen compounds can be competitive to sulfur for the active sites of activated carbon. It is highly needed to develop a new process, which aims at more selective removal of sulfur compound using AC amidst other impurities for effective desulfurization with acceptable fuel quality[1].

3. Previous Reviews

A comparison between some recent and prominent scientific reviews on Adsorptive Desulfurization (ADS), especially using Activated Carbon (AC) or other adsorbents is given table 7 below. This table is designed to serve as a guide to the scope, major aspects and strengths and weaknesses of each review so as to highlight the scientific novelty of the present manuscript.

Table 7: previous reviews on Activated Carbon (AC) adsorptive desulfurization (ADS).

Limitations / Gaps	Key Features	Main Focus / Scope	Year	Reference
Outdated; does not cover recent advancements in AC surface engineering.	Comprehensive overview of HDS, ODS, BDS, and ADS.	General desulfurization technologies.	2012	[77]

Focus is spread across many materials; lacks deep dive into specific AC modifications.	Detailed mechanisms of adsorption on various materials.	Broad range of adsorbents (MOFs, Zeolites, Carbons).	2016	[78]
Narrow scope (only rubber-derived AC); lacks recent literature (post-2016).	Focus on waste valorization for ADS.	Waste-derived AC (specifically rubber tires).	2016	[79]
More of a research/evaluation paper than a comprehensive review of literature.	Economic applicability and performance comparison.	Evaluation of AC from various sources.	2020	[41]
Focuses primarily on biomass; may lack focus on synthetic or nano-structured ACs.	Insights into processes, modifications, and regeneration.	Biomass-derived AC for ADS.	2023	[9]
Does not focus on Activated Carbon.	Comprehensive review of metal-modified zeolites.	Zeolite-based adsorbents for ADS.	2025	[80]
Does not focus on Activated Carbon.	Latest achievements in MOF-based desulfurization.	MOFs in ADS.	2026	[83]

Although many reviews on Adsorptive Desulfurization (ADS) with different adsorbents have been published, it is obvious that a comprehensive and up-to-date review is still missing in the literature that focuses on the recent developments of AC for ADS, especially for gasoline application. Most of the previous reviews are old [77], are very broad [78] or deal with very specific types of AC such as waste [79] and biomass [9] or are not focused on activated carbon [80]. The content of this manuscript is unique due to its extensive and modern review on the advances in gasoline adsorptive desulfurization using activated carbon, published up to 2026. Unlike previous reviews, this manuscript:

- Compiles and categorizes the latest innovations in AC Feed-stocks, highlighting sustainable sources and ecological and economic considerations.
- Comprehensively reviews the surface modification approaches of AC such as physical, chemical (including oxidation/reduction and nitrogen doping) and biological modification with the influence on the adsorption capacity and selectivity.
- Decreases the number of components in gasoline that can interact with AC (adsorption mechanos describes how the various species interact and provides extensive understanding of the adsorption process). Outlines the principal challenges that remain including poor adsorption capacity, and the absence of regeneration and selectivity with different inhibitors, and discusses future prospects for increasing molecule manufacturing levels as a potential route of realization of ultra-low sulfur fuels for AC based ADS system design and deployment.

This manuscript will be an invaluable resource for those researching in this area, with a dedicated focus and modern analysis, incorporating the latest in Feed-stocks, modification methods (including biological modifications), interaction mechanisms, challenges and future prospects. It provides a different point of view that accentuates the novelty and progress in science that is not adequately reviewed elsewhere, particularly for gasoline desulfurization.

4. Prospective Trajectories

The future of activated carbon (AC) in gasoline desulfurization should move beyond basic laboratory experiments into applied, scalable and industry relevant models. The following specific research directions and testable hypotheses are proposed in order to deal with current limitations.

10.1 Advanced Modification and Testable Hypotheses.

Future studies should go beyond the generic, surface-based modifications, to the design of smart adsorbents with active sites that are tailored.

- **Hypothesis 1**: When transition metal-organic frameworks (MOFs) are incorporated into the AC matrix, there will be the formation of a hierarchical pore structure which reduces the intra-particle diffusion resistance by at least 30% relative to the virgin AC, in specific with respect to bulky sulfur molecules such as dibenzothiophene (DBT)[10].
- **Hypothesis 2:** Surface functionalization with a specific set of nitrogen-rich ligands (e.g., pyridinic-N) will increase the π-complexation between the adsorbent and thiophenic rings, and selectivity coefficient of sulfur over aromatics (e.g., benzene/toluene) by a factor of 2 or more[72].

10.2 Regeneration Investigations and Cyclic stability.

The limitation of recyclability of AC is a critical barrier to its industrial adoption. The future research should focus on the energy-saving regeneration procedures.

- **Thermal vs. Solvent Regeneration**: Comparative studies are needed to evaluate the efficiency of thermal regeneration (e.g., under N2 at 400–600°C) versus solvent-assisted regeneration (e.g., using ethanol or n-octane)[74].
- **Cyclic Performance:** Research should report the desulfurization capacity over at least 10–20 adsorption-regeneration cycles. One of the aims is to find methods of modifying the structure to retain more than 90 percent of the original capacity after many cycles to overcome the common problem that pore blockage by carbonaceous deposits or sulfur oxidation products[81].

10.3 Real Gasoline Testing and Competitive Adsorption.

Most of the literature presently available is based on the use of so-called model fuels (e.g., thiophene in n-octane), which are not representative of the complexity of industrial gasoline.

- **Complex Matrices:** Future experiments require the use of real FCC (Fluid Catalytic Cracking) gasoline, which contains olefins, aromatics and moisture, which compete to occupy adsorption sites[9].
- **Interference Analysis:** Research ought to measure the effect of co-existing hydrocarbons on the removal of sulfur as an inhibitory effect. As an example, testing the effect of the presence of 20% aromatics in decreasing the break-through time of sulfur compounds will give the data necessary to design robust industrial-scale adsorbers[73].

10.4 Sustainability and Economic Scalability.

Life-cycle assessments (LCA) should be used to support the transition to bio-based activated carbon to ensure economic viability.

- **Waste-to-Wealth:** Future directions must be concerned with maximizing the surface areas of agro-wastes (e.g., date pits, rice husks) to a surface area of over 1500 m2/g and at a cost less than 1.5/kg[82].
- **Process Integration:** The work of exploring how AC adsorption can be integrated into a process that could achieve <10 ppm sulfur levels at significantly reduced hydrogen use and operating costs may prove to be an intriguing approach[82].

10.5 Advanced Characterization and Mechanistic Understandings.

The proposed hypotheses should be verified with the help of advanced characterization. The methods to be used to monitor the changes occurring in the functional groups on the surface as the adsorption process progresses should include In-situ DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy). This will enable researchers to differentiate the physical adsorption and chemisorption processes, and guide the rational design of the next generation of desulfurization adsorbents[82].

5. Conclusion

Adsorptive desulfurization using activated carbon is one of the most promising technologies for producing ultra-low sulfur gasoline with less severe and more sustainable operating conditions as compared to hydrodesulfurization. Recent studies have been analyzed and the adsorption capability of activated carbon is strongly influenced by its surface area, pore structure and surface chemistry, and the modification of the carbon by heteroatoms and chemical modification greatly increases the sulfur selectivity towards refractory compounds like dibenzothiophene and its derivatives.

The reviewed literature also emphasizes that the use of sustainable precursors is becoming increasingly important, especially agricultural and waste products (date pits, coconut shells, waste tires, biomass residues etc.) with competitive adsorption performance and lower production costs and environmental effects. Moreover, the incorporation of metal-functionalized activated carbon and advanced surface engineering methods has demonstrated great potential to enhance the adsorption capacity, selectivity, and regeneration properties.

Although significant progress has been made, there are still significant challenges to overcome before adsorbent use can be scaled up for industrial use, such as adsorbent deactivation, competitive adsorption within actual real gasoline matrices, regeneration efficiency, and long-term cyclic stability. In this context, further studies are needed to develop highly selective multifunctional adsorbents, to optimize the approaches to regeneration, and to validate the adsorption systems in real industrial conditions, using real fuel streams instead of model fuels.

In summary, the use of activated carbon for adsorptive desulfurization of transportation fuels is a technically viable and environmentally friendly option. The technology is poised for further development towards laboratory-to-industry use that can realize global ultra-low sulfur fuels, with continued improvements expected in synthesis of sustainable adsorbents, understanding of the mechanisms, and the scaling up of processes.

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Reference

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