

Research Article



Desulfurization of Zawia Refinery Diesel Using Adsorption Fixed Bed Process

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Abstract: The study focuses on the dynamic modeling of a fixed-bed adsorber for the adsorption of sulfur compounds in diesel fuel. The model considers non-ideal plug flow behavior and velocity variation along the column, providing a more realistic representation of the adsorption process. Additionally, internal mass-transfer resistances due to pore diffusion mechanisms are incorporated into the model. The study investigates adsorption performance by examining different flow rates (5 cc/min, 10 cc/min, 15 cc/min, and 20 cc/min) and inlet concentrations ranging from 586 to 100 ppm. The bed height is constant at 30 cm. The behavior of various parameters, such as bed utilization, breakpoint time, film mass transfer coefficient, and height of the adsorption zone, is analyzed. The results indicate that a sharp front of the breakthrough curve is observed, followed by the broadening of the tail of the breakthrough curve. The breakthrough curve represents the adsorbate concentration in the effluent stream over time. The investigation reveals that a high flow rate of 20 cc/min and a high inlet concentration yield better overall bed capacity utilization for the adsorption system. This means that the bed is more effectively utilized at higher flow rates and higher inlet concentrations, leading to improved adsorption performance. In conclusion, high flow rates and high inlet concentrations are favorable for enhancing the adsorption system's performance in terms of bed utilization. These results provide valuable insights for optimizing the design and operation of fixed-bed adsorbers that remove sulfur compounds from diesel fuel.

Keywords: Dynamic Modeling; Fixed-Bed Adsorber; Mass-Transfer Resistances; Sulfur Compounds; Sulfur Removing.

1. Introduction

Sulfur poses a significant challenge to environmental preservation and transportation equipment's optimal functioning. Consequently, regulations have been implemented to restrict sulfur levels in fuel for on-road vehicles to 30 parts per million (ppm) to mitigate its detrimental effects [1], [2]. This impurity can potentially deactivate catalysts by poisoning their active sites, resulting in considerable costs associated with maintenance and replacement.

Soon, a promising frontier emerges in the form of fuel cells that require ultra-low sulfur content, typically below ten parts per million (ppm), with the potential for even lower concentrations [3], [4]. These advanced fuel cells can produce ultra-clean fuel using fixed-bed selective adsorption techniques. This innovative approach

addresses the stringent sulfur requirements for optimal fuel cell performance and offers the prospect of enhancing environmental sustainability and energy efficiency [5].

Researchers have increasingly recognized the importance of ultra-low sulfur content in fuel for various applications, including fuel cells. By minimizing sulfur impurities to deficient levels, these fuel cells can operate more efficiently and with excellent reliability, improving overall performance and longevity [6], [7]. Using fixed-bed selective adsorption technology significantly advances sulfur removal from fuel. This process involves the selective capture of sulfur compounds from the fuel stream, ensuring that only ultra-clean fuel reaches the fuel cell, thereby mitigating the risk of catalyst poisoning and maximizing energy conversion efficiency [8], [9].

Nitrogen compounds exhibit a significantly more inhibitory effect at equimolar concentrations than

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polycyclic aromatic hydrocarbons (PAHs). This observation underscores the importance of considering the differential impacts of various impurities when designing adsorption processes for fuel purification. Computational simulations of multicomponent breakthrough curves, leveraging the ideal adsorbed solution theory and the linear driving force model, demonstrate excellent agreement with experimental data. These simulations provide valuable insights into the mass transfer dynamics governing the removal of impurities from the fuel stream.

A combination of liquid film diffusion and pore diffusion mechanisms primarily governs the mass transfer process. Likely, the mass transfer occurs initially from the liquid phase into macro- or mesopores before further adsorption occurs in micro-pores. This sequential transfer process highlights the complex interplay between molecular diffusion and adsorption kinetics within the porous structure of the adsorbent material.

The design of the fixed bed column for diesel fuel purification demonstrates a robust relationship between the liquid hourly space velocity (LHSV) and the ratio of dibenzothiophene to the total adsorption amount. This relationship indicates the adsorption process's efficiency and effectiveness under varying flow conditions [10]. By optimizing the LHSV, it is possible to achieve maximal removal of sulfur-containing compounds such as dibenzothiophene while maintaining operational stability and throughput in the purification system.

Granular activated carbons (GAC) are highly versatile adsorbents used across various industries for their effectiveness in liquid mediums. They are available in powdered or granular forms spanning a range of 0.2 to 5 mm. The intricate process of adsorption on activated carbons (AC) arises from a complex interplay between the AC's surface properties and the adsorbate molecules [11], [12]. This interaction is further delineated into two main categories: electrostatic and non-electrostatic.

Electrostatic interactions come into play when the adsorbate is an electrolyte, which undergoes dissociation into ions within the solution. Depending on variables such as the charge density and the Point of Zero Charge (pHPZC) of the activated carbon and the chemical composition and characteristics of the adsorbate, these electrostatic interactions can be attractive or repulsive. On the other hand, non-electrostatic interactions are inherently attractive and encompass various forces such as van der Waals forces, hydrophobic interactions, π - π interactions, and hydrogen bonding [13], [14].

Determining the breakthrough curve is essential for establishing a practical scale of column adsorption, which is crucial for various applications. Two primary approaches are widely employed for obtaining the breakthrough curve of an adsorption system: direct experimentation and

mathematical modeling [15]. Direct experimentation yields a direct and concise breakthrough curve for a given system. However, it is often time-consuming and economically unfavorable, especially for scenarios involving trace contaminants or long residence times. Additionally, experimental outcomes heavily rely on ambient temperature and residence time [16], [17].

This study focuses on mathematical adsorption modeling within a packed bed utilizing a porous adsorbent, executed and solved through MATLAB programming. The control volume method is employed to approximate the derivatives in the convection term, derived from the partial differential equation governing the mass transfer process, which dominates the mass transfer step. This model incorporates considerations for film mass transfer resistance, non-ideal plug flow, and fluid velocity variation along the bed [18], [19].

The study further investigates the effects of design and operational parameters, including flow rate, inlet concentration, and bed height, on the degree of bed utilization. This analysis provides valuable insights into optimizing adsorption processes for enhanced efficiency and effectiveness.

2. Material and Methods

2.1. Mass Transfer Modeling

In this study, mass transfer modeling is crucial in predicting and correlating physical processes [20]. Two primary mechanisms contribute to mass transport in the bulk phase: convection along the column's axial direction and axial dispersion. Molecules within the bulk interstitial phase are transported to the particle surface via axial convection and friction diffusion, commonly called film diffusion. Once at the surface, molecules can further diffuse into the inner portion of the particle through surface diffusion, pore diffusion, or a combination of both [21], [22].

The focus of this study lies in comprehending the mechanism of pore diffusion, as well as considering mass transfer resistance and non-ideal plug flow along the column. Although the variation in fluid velocity along the bed was initially neglected in predicting breakthrough curve behavior due to internal mass transfer resistances and non-ideal plug flow, the current study modifies this model by incorporating velocity variation along the column [23]. This modification is essential for providing a more comprehensive understanding of the mass transfer dynamics within the packed bed. By accounting for fluid velocity variation, the model can better capture the intricacies of mass transport phenomena, ultimately

enhancing the accuracy of predictions regarding breakthrough behavior [24].

2.1.1. Assumptions Model

To develop a generalized model corresponding to the pore diffusion mechanism, adhering to the specified assumptions, we can proceed as follows:

- **Isothermal Conditions:** The system operates under constant temperature conditions for both the fluid and solid phases.
- **No Pressure Drops:** There are no variations in pressure throughout the column, ensuring uniformity in flow conditions.
- **No Chemical Reactions:** Chemical reactions do not occur within the bed, simplifying the model to focus solely on adsorption phenomena.
- **Langmuir Adsorption Isotherm:** The adsorption equilibrium follows the Langmuir isotherm model, which describes a nonlinear relationship between adsorbate concentration and adsorption capacity.
- **Variation in Fluid Velocity:** The fluid velocity changes along the column, affecting the mass transfer coefficient.
- **Linear Driving Force (LDF) Approximation:** Mass transfer between the fluid and solid phases is approximated using the linear driving force model, assuming a linear relationship between concentration gradients and mass transfer rates.
- **Characterization of Mass Transfer Across Boundary Layers:** Mass transfer across the boundary layer surrounding the solid particles is accounted for, considering the influence of concentration gradients on diffusion rates.

Combining these assumptions, we can formulate a generalized model to describe the pore diffusion mechanism in the system. This model will solve partial differential equations governing mass transfer within the porous medium, incorporating boundary conditions and parameters such as pore diffusion coefficients, Langmuir constants, and mass transfer coefficients. The resulting model will provide insights into the dynamics of adsorption processes within the packed bed under consideration.

2.1.2. Simulation Technique

Incorporating the consideration of nonlinear adsorption equilibrium, the series of partial differential equations (1 to 9) mentioned earlier is tackled numerically by transforming it into a set of ordinary differential equations via the Explicit Finite Difference technique. This method, as evidenced by previous studies conducted by Babu and

Chaurasia [25]–[33], has been effectively employed in similar contexts. A robust mathematical algorithm is formulated to address this interconnected set of equations, subsequently implemented into a computer program using MATLAB (Version 20) software. This computational tool is a powerful means to simulate and analyze the complex dynamics inherent in the adsorption process.

Building upon the foundational assumption regarding the control volume, which asserts that the product of the area (A) and the incremental change in Z (dZ) is equal to the volume (V), as illustrated in Figure 1, particularly in scenarios where Z approaches 0, facilitates the determination of the rate of accumulation or depletion. This insight is pivotal in understanding the nuanced behavior of the system and optimizing its performance.

$$Dl \frac{\partial C_b}{\partial Z^2} + V \frac{\partial C_b}{\partial Z} + Cb \frac{\partial V}{\partial Z} + \frac{\partial C_b}{\partial t} + \rho p \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial qp}{\partial t} = 0 \quad (1)$$

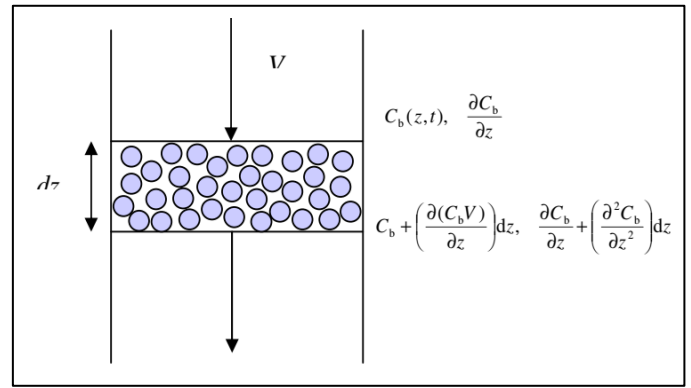


Figure 1. Mass Balance in Element of Fixed Bed.

The subsequent equation gives the contour forms at both ends of the column:

$$D_L \frac{\partial C_b}{\partial Z^2} = -V(C_{bo} - C_b); \quad Z = 0; t > 0 \quad (2)$$

$$\frac{\partial C_b}{\partial Z^2} = 0; \quad Z = 1; t \geq 0 \quad (3)$$

In fixed bed adsorption, the superficial velocity (V) undergoes variation along the axial direction of the bed due to the adsorption process. To estimate (dv/dz) , we utilize the following equation, which considers the fluctuation of the velocity of the bulk fluid as it progresses along the axial direction of the bed during liquid adsorption, assuming constant liquid density. This enables us to derive the total mass balance equation.

$$\rho_L \frac{\partial v}{\partial z} = -(1-\varepsilon)\rho_s \frac{\partial qp}{\partial t} \quad (4)$$

Velocity Boundary Condition: The diffusion of adsorbate molecules through the pore governs the intra-pellet mass transfer. The macroscopic conservation equation representing this process is as follows:

$$\varepsilon_p \frac{\partial C}{\partial t} + (1 - \varepsilon_p) \rho_p \frac{\partial q}{\partial t} = D_p \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (5)$$

Assuming instantaneous equilibrium

$$\frac{\partial q}{\partial t} = \frac{\partial C}{\partial t} \frac{\partial q}{\partial C} \quad (6)$$

The requirement for symmetry at the core of the particles and the need for continuity on the outer surface of the adsorbent bed are stated as follows:

$$\frac{\partial C_b}{\partial Z^2} = 0; \quad Z = 1; t = 0 \quad (7)$$

$$K_f(C_b - C_s) = D_p \frac{\partial C}{\partial r} \quad r = a_p; t > 0 \quad (8)$$

The adsorption isotherm exhibited favorable and nonlinear behavior, following the Langmuir Isotherm model [34].

$$q = \frac{q_m b_c}{1 + b_c} \quad (9)$$

2.2. Samples and Experimental Techniques

This part deals mainly with preparing the samples and experimental techniques to determine the kinetic (dynamics) behavior of fixed bed adsorbers. Furthermore, the characteristic breakthrough curve of the adsorption phenomena can be obtained through mathematical models. The experimental measurement of fixed bed adsorption column must accomplish concentration with time, take concentration after of time in all steps and then measure concentration by x-ray.

2.2.1. Samples and Analysis

Diesel Oil: The diesel oil utilized in this study was meticulously sourced from a shore tank located within the premises of the Az-Zawiya oil refining company, a prominent entity within Libya's oil industry. Known for its stringent quality control measures, the Az-Zawiya refinery ensures its products meet rigorous standards. Upon procurement, the diesel oil exhibited an initial sulfur content of 627 parts per million (ppm), a vital metric for assessing its environmental impact and suitability for various applications.

Carbon Materials: The carbon material employed in this study, specifically granular activated carbon (GAC), exhibited a cylindrical form with a diameter of 2mm and a height of 5mm. Selected as the sorbent material for sulfur compounds, this GAC configuration offers an optimal balance of the surface area, porosity, and mechanical stability, crucial for efficient adsorption processes.

The instrument for Analysis: To accurately assess the sulfur content and identify heavy metal contaminants within the diesel fuel samples, the study employed the X-Supreme 8000 Benchtop XRF Analyzer, manufactured by Hitachi Group Limited, a renowned Japanese corporation known for its cutting-edge analytical instruments. The X-Supreme 8000 XRF Analyzer offers precise and reliable elemental analysis capabilities, making it an ideal choice for comprehensively characterizing diesel fuel samples. It is non-destructive nature, and rapid analytical speed allows efficient sulfur content and heavy metal concentration screening without complex sample preparation procedures.

In this study's adsorption (exhaustion) experiments, calcium emerged as the predominant element observed in the exhausted granular activated carbon (GAC) samples. This observation suggests that calcium compounds were effectively adsorbed onto the GAC surface during the experimental process. The prevalence of calcium in the exhausted GAC samples indicates its significant role in the adsorption mechanism, potentially displacing or interacting with sulfur compounds in diesel fuel. Understanding the elemental composition of the exhausted GAC samples provides valuable insights into the adsorption behavior and effectiveness of the GAC material in removing sulfur compounds and other impurities from diesel fuel.

2.2.2. Experimental Procedures

Experimental Adsorption Isotherm Data: An isotherm study has further investigated the equilibrium data that helps describe the relationship between the liquid phase (adsorbate concentration) and the solid phase (adsorbent) at constant temperature and helps design the adsorption systems.

Column operations (T=25 C, P=1 atm) [20]. The desulfurization process for getting through the curve of adsorption phenomena can be obtained through mathematical models. Figure 2 shows a schematic diagram of the fixed bed adsorption process during the adsorption process. The fluid passes through the back of the adsorbent to transfer the adsorbate from the feed to the solid as the fluid continuously drains the adsorbent. Saturated from the adsorbate molecules and creates an absorption zone bed in the bed.

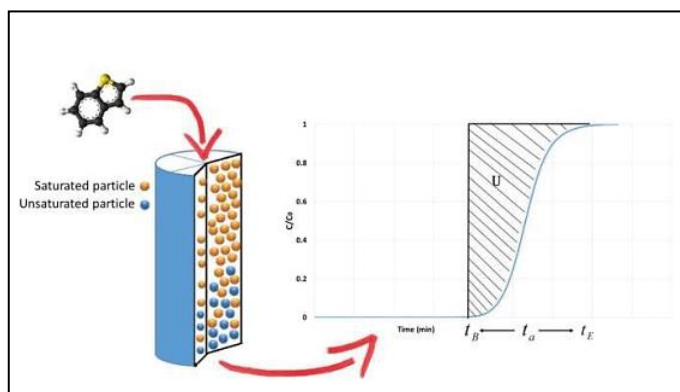


Figure 2. Adsorption Process Scheme and Concentration Profile.

Adsorption occurs due to the bonds formed between atoms of the same substance and their neighboring atoms, facilitated by natural attractive forces such as Vander Waals [35]. Under appropriate pressure and temperature conditions, multiple layers of the adsorbent material can form on the surface of the adsorbent material. Unlike high-temperature processes, this adsorption type occurs at low temperatures and does not require activation energy. The interaction between the adsorbent surface and the adsorbed particles is influenced by various factors such as the shape, size, radius, polarity, presence of functional groups, molecular weight, and solubility of the adsorbent [36]–[38].

In a solution containing multiple components, selective adsorption of one component over the others can occur. Increasing the molecular weight of the adsorbent enhances its adsorption process by providing more opportunities for association with the surface at multiple sites. Adsorbents with multiple aromatic rings are particularly effective in enhancing adsorption efficiency on various surfaces and promoting their distribution in terms of regularity or homogeneity across the surface. The adsorption efficiency relies heavily on the physical and chemical properties and the particle size of the adsorbent material. Decreasing particle size increases the adsorption rate by facilitating the diffusion step on the material's surface. Therefore, smaller particles enhance the diffusion process, a critical aspect of adsorption [39]–[42].

3. Result and Discussion

The study employs a model to determine outlet adsorbate concentrations under various operating conditions, detailed in Table 1, while considering linear velocity variations along the bed for comparison with prior research [43]–[45]. Investigation into the impact of feed flow rates, conducted with constant parameters, is depicted in Figure 3 for three different flow rates. As

observed, increasing flow rates result in steeper breakthrough curves, indicating the quicker exit of the adsorbate solution from the column before equilibrium. Moreover, maintaining a fixed saturation capacity of the bed under the same driving force, higher flow rates lead to shorter saturation times. For instance, at a flow rate of 20 cc/min, the breakpoint time is determined to be 8 minutes. This comprehensive analysis highlights the interplay between flow rates and adsorption dynamics, providing insights crucial for optimizing adsorption processes.

Table 1. Model Parameters Value for Simulation

Sym	Parameter	Value
ϵ	Bed porosity	0.35
ρ_L	Liquid density (kg/lit)	0.8403
D_L	Axial dispersion coefficient (m^2/s)	3×10^{-4}
q_m	maximum adsorption capacity (mg/g)	2×10^{-4}
b	Langmuir isotherm constant (ml/mg)	2.5×10^{-5}
K_f	External mass transfer coefficient (m/sec)	3×10^{-5}
D	Bed diameter (cm)	1.10

These findings highlight the significance of flow rate in the desulfurization process. Higher flow rates result in faster breakthroughs and reduced time for saturation, indicating the need for careful consideration of flow rate in the design and operation of the adsorption column. By considering linear velocity variation along the bed, the model provides a more realistic representation of the adsorption process and allows a better understanding of its behavior under different flow rate conditions. The comparison of results with previous research further validates the model and enhances its credibility in predicting the outlet adsorbate concentration at varying time intervals.

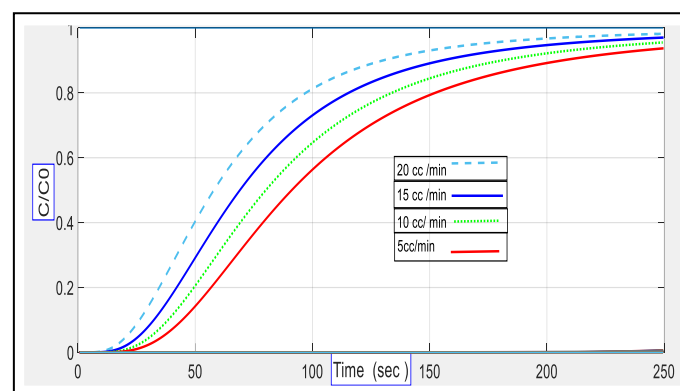


Figure 3. Effect of Flow Rates on Breakthrough Curves

Breakthrough Curve Behavior: As mentioned earlier, the breakthrough curve becomes steeper as the flow rate

increases. This indicates that a higher flow rate results in a more rapid breakthrough of the adsorbate, leading to a shorter breakthrough time. The breakthrough time refers to the time it takes for the adsorbate concentration in the effluent stream to exceed a specified threshold or regulatory limit.

Saturation Time: With a fixed saturation capacity of the bed based on the same driving force, an increase in flow rate leads to a shorter time for bed saturation. This means the bed reaches its adsorption capacity at higher flow rates more quickly. Consequently, the breakthrough of the adsorbate occurs earlier, resulting in a shorter breakthrough time (Figure 4)

Importance of Linear Velocity Variation: Considering the linear velocity variation along the bed is crucial for accurately modeling the adsorption process. In reality, the velocity of the fluid flowing through the bed is not constant along its length. Factors such as fluid distribution, pressure drop, and adsorbent packing irregularities can cause variations in linear velocity. Considering these model variations, a more realistic representation of the adsorption process and the resulting breakthrough curve can be obtained.

By analyzing the impact of flow rate and incorporating the consideration of linear velocity variation, engineers and researchers can make informed decisions in designing and optimizing adsorption processes. The findings help determine the appropriate flow rate that balances efficient adsorbate removal and optimal bed utilization while considering the desired breakthrough time and regulatory requirements.

Moreover, validating the model through comparison with previous research enhances its credibility. It shows reliability in predicting better behavior and reason for GAC activity and diesel concentration and obtaining the breakthrough curve under different flow rate conditions. This knowledge helps us design and operate adsorption systems for desulfurization and other applications at the lowest linear velocity variation.

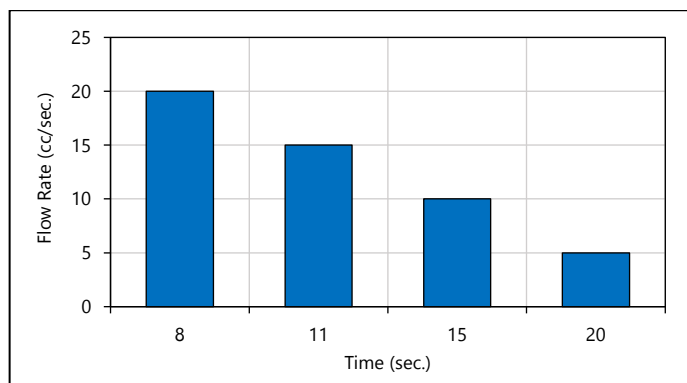


Figure 4. Breaks Through Curves at Different Flow Rates.

The investigation conducted on the effect of flow rate, inlet concentration, and bed height on the behavior of the breakthrough curve revealed that these parameters play significant roles in the design and operation of the packed bed column. The study employed the method of lines for solving the partial differential equation (PDE) governing the adsorption bed, which yielded accurate results. Additionally, this method demonstrated both high accuracy and a reasonable convergence rate.

The optimum flow rate value depended on the flow direction, bed dimensions, and inlet concentration. Increasing the flow rate resulted in a steeper slope of the breakthrough curve and a decrease in the breakpoint time. Moreover, a high inlet concentration led to a decrease in the degree of bed saturation. It should be noted that the bed height was kept constant at 30 cm. The increased bed height impacted the resistance to mass transfer and influenced the time required to reach adsorption equilibrium.

These findings are significant when compared to the results of a previous study [15], [46]–[48], as they consider factors such as viscosity, diesel type, density, and pore diffusion (GAC). Overall, the results obtained from this investigation provide valuable insights for the comparison and analysis of different desulfurization studies, considering the various parameters and conditions involved.

The flow rate of the inlet stream significantly influences the breakthrough curve dynamics. An increase in the flow rate typically yields a sharper incline in the breakthrough curve. This indicates a more rapid breakthrough of sulfur compounds, resulting in a shorter breakthrough time. Conversely, a lower flow rate tends to produce a more gradual slope in the breakthrough curve, extending the breakthrough time duration. This observation aligns with findings from previous studies [49], [50], which underscore the direct relationship between flow rate variations and breakthrough curve characteristics in packed bed adsorption processes.

The inlet concentration of sulfur compounds in the incoming stream, often referred to as the inlet concentration, plays a pivotal role in shaping the behavior of the breakthrough curve. A higher inlet concentration exerts a notable influence, resulting in a more pronounced breakthrough curve characterized by a steeper slope and an earlier occurrence of breakthrough. This phenomenon occurs because a higher concentration signifies an increased influx of sulfur compounds into the bed, hastening the saturation of the adsorbent material. This observation aligns with studies conducted by researchers such as [51], [52], highlighting the significant impact of inlet concentration variations on breakthrough curve characteristics in adsorption processes.

The height of the packed bed column significantly affects the breakthrough curve's behaviour. Keeping the bed height constant while increasing it results in a longer breakthrough time. This is because a taller bed height increases the resistance to mass transfer, thus delaying the sulfur compounds' attainment of adsorption equilibrium. Consequently, the breakthrough curve exhibits a more gradual slope. This observation aligns with findings from studies like [53], [54], which emphasize the crucial role of bed height variations in shaping breakthrough curve dynamics in adsorption processes.

It is important to note that these factors are interrelated, and their combined effect impacts the desulfurization process in the packed bed column. The optimal values for flow rate, inlet concentration, and bed height depend on several factors, including the system's specific design and operating conditions, the desired desulfurization level, and the adsorbent material characteristics. By studying the behavior of the breakthrough curve and considering these factors, engineers and researchers can make informed decisions regarding the design and operation of packed bed columns for the effective desulfurization of diesel fuel. Based on the study's findings, it can be inferred that high flow rates and high inlet concentrations are favorable for enhancing the adsorption system's performance in terms of bed utilization. These results provide valuable insights for optimizing the design and operation of fixed-bed adsorbers that remove sulfur compounds from diesel fuel.

4. Conclusion

From the research findings, it can be concluded that factors such as flow rate, inlet concentration, and bed height play significant roles in the behavior of the breakthrough curve in packed bed columns. The application of the method of lines to solve the partial differential equation (PDE) governing the adsorption bed yielded accurate results, demonstrating high accuracy and a reasonable convergence rate.

The optimal flow rate depended on the flow direction, bed dimensions, and inlet concentration. Increasing the flow rate resulted in a steeper breakthrough curve and a shorter breakthrough time. Furthermore, a high inlet concentration led to a decrease in the degree of bed saturation. The increased bed height impacted mass transfer resistance and influenced the time required to reach adsorption equilibrium. Considering viscosity, diesel type, density, and pore diffusion (GAC) factors, these conclusions are important. The research findings provide valuable insights for comparing and analyzing different desulfurization studies, considering various parameters and conditions involved.

In practice, this research provides valuable guidance for engineers and researchers to make informed decisions regarding designing and operating packed bed columns for diesel fuel desulfurization. Based on the study's findings, it can be inferred that high flow rates and high inlet concentrations are favorable for enhancing the performance of the adsorption system in terms of bed utilization. These conclusions offer valuable insights for optimizing the design and operation of fixed-bed adsorbers for removing sulfur compounds from diesel fuel.

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