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Research Article

Enhancing Denitrification And Cod Removal In Spouted Bed Reactors: A Modeling Approach To Optimize Mass Transfer And Biofilm Dynamics.

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Abstract

This study explores the optimization of denitrification and Chemical Oxygen Demand (COD) removal in spouted bed reactors (SBRs) by modeling mass transfer and biofilm dynamics under aerobic conditions. The research examines the impact of varying Granular Activated Carbon (GAC) masses and flow rates on treatment efficiency. Results indicate that higher flow rates enhance COD removal, while lower flow rates improve nitrate reduction. Scanning Electron Microscopy (SEM) analysis revealed biofilm thicknesses ranging from 3.22 to 7.02 µm, significantly influencing mass transfer and treatment outcomes. A developed model highlighted the inverse relationship between mass transfer coefficients and both flow rate and GAC loading, emphasizing the need for precise optimization. These findings provide valuable insights into enhancing wastewater treatment processes using SBRs, contributing to improved environmental sustainability.

Keywords : Spouted Bed Reactor, Denitrification, Chemical Oxygen Demand (COD) Removal, Mass Transfer Optimization, Biofilm Thickness, Granular Activated Carbon (GAC), Wastewater Treatment, Scanning Electron Microscopy (SEM), Modeling and Simulation.

INTRODUCTION

Wastewater treatment is a critical aspect of preserving environmental quality and sustaining ecosystems [5]. The urgent need to address the global concern of nitrate contamination in industrial wastewater necessitates effective and eco-friendly treatment methods [1]. This comprehensive study focuses on denitrification within a spouted bed reactor (SBR) under aerobic conditions, presenting a promising technology for simultaneous nitrate removal. Four key objectives guide this research, aiming to enhance the efficiency and understanding of denitrification processes.

The performance of an SBR in removing nitrates from industrial wastewater under aerobic conditions. Achieving nitrate removal under aerobic conditions is vital for simultaneous organic matter reduction, contributing to environmental sustainability [1]. Remarkable results showcase substantial reductions, nitrates and total chemical oxygen demand (COD), emphasizing the critical role of residence time in treatment efficacy.

Biofilm development and microbial kinetics within the reactor, acknowledging the fundamental role of microbial communities in denitrification processes [7]. The study also investigates the production of extracellular polymeric substances (EPS) by microorganisms, shedding light on their contribution to enhanced denitrification.

The mass transfer resistance within the spouted bed reactor, crucial for addressing limitations and enhancing denitrification efficiency [6]. The reactor's design, creating distinct aerobic and anoxic zones, facilitates simultaneous denitrification and COD reduction. Developing an empirical model to represent denitrification within the SBR, providing a valuable tool for predicting and optimizing performance [8].

This research significantly contributes to wastewater treatment technologies and environmental sustainability, offering insights into denitrification processes within spouted

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bed reactors. The findings serve as a valuable reference for researchers and engineers seeking to improve denitrification in industrial wastewater treatment systems.

MATERIALS AND METHODS

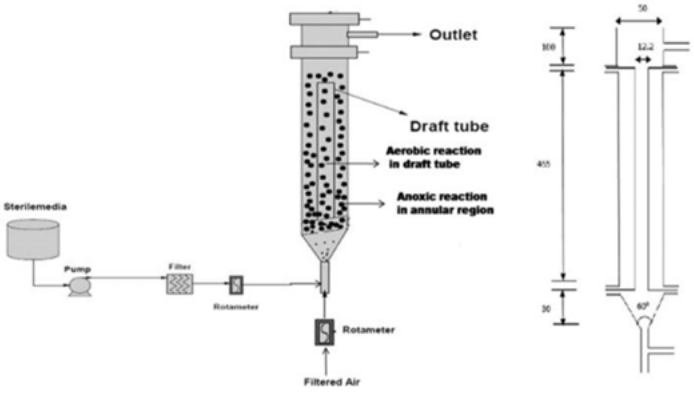
Materials

The sludge source was obtained from the Madihal Sewage Treatment Plant, and a 5L nutrient media comprising dextrose, potassium nitrate, magnesium sulfate, ferrous sulfate, potassium di-hydrogen phosphate, and calcium chloride was prepared. Initial incubation involved transferring 5L of nutrient media to 5L of sludge. Subsequent culture management included removing the top 5L of the 10L culture, mixing it with 5L of fresh media, and incubating for 48 hours. This cycle was repeated cumulatively for up to 144 hours. Microscopic analysis confirmed the enormous arrangement of Pseudomonas spp., signifying successful adaptation. GAC particles (2.4 mm) were then introduced to the sludge, and after 48 hours of room temperature incubation with occasional stirring, a biofilm was observed on the GAC surface.

The spouted bed reactor setup involved a 2-inch cylindrical column made of polyvinyl chloride (PVC) with a central 1-inch draft tube, operating continuously for 24 hours. Wastewater, replicating the higher average composition of municipal wastewater, was introduced via a funnel, containing an initial total Chemical Oxygen Demand (COD) of 600 mg/L and nitrate concentration of 40 mg/L. Controlled aeration with compressed air through a filter-initiated spouting of solids within the draft tube, with experiments conducted until a stable state was achieved. Four dilution rates (1.2 l/h, 1.8 l/h, and 2.4 l/h) were applied, each with a..... 15 g loading of Granular Activated Carbon (GAC). Systematic experimentation continued until a reproducible state was attained at specified dilution rates, ensuring reliable results. Effluent samples collected at intervals underwent analysis, focusing on COD removal by oxidation in the draft tube, utilizing atmospheric oxygen, and denitrification in the annular section with carbon serving as the electron donor. This meticulously designed experimental approach aimed to explore the impact of various dilution rates on COD and nitrate removal in a spouted bed reactor, incorporating GAC as a crucial component, providing a comprehensive understanding of treatment efficiency under diverse conditions.

Experimental setup

Figure 1.



SEM Analysis

SEM played a crucial role in this study, scanning samples with an electron beam to generate magnified images for in-depth analysis. By utilizing a focused beam of high-energy electrons, SEM produced signals at the surface of solid specimens, enabling data collection over specific areas. The resulting two-dimensional images displayed spatial variations in properties like chemical characterization, texture, and material orientation. SEM also conducted analyses at specific points on the sample, with signals originating from electron interactions at different depths, including secondary electrons (SE), reflected signals, characteristic X-rays, absorbed light current, and transmitted electrons. While secondary electron detectors were standard, not all machines featured detectors for other signals. Meeting SEM requirements involved preparing small samples for the specimen stage, enhancing electrical conductivity and stability. Typically mounted on a conductive adhesive on a specimen holder or stub, SEM found extensive use in semiconductor wafer defect analysis, capable of examining any part of a 300 mm wafer. Instruments

often featured chambers allowing tilting and continuous 360° rotation of objects. Backscattered electrons (BSE), crucial for SEM analysis, consisted of high-energy electrons reflecting out of the specimen, providing contrast based on scattering characteristics and revealing areas with different chemical compositions.

External mass transfer coefficient using bio mass model

Fixed Parameters

The following parameters were fixed throughout the study:

1. Cross sectional area of the reactor = 0.00196 m2
2. Diffusivity of substrate in the bio film (from literature) = D = 8.15×10^{-10} m2/s
3. Reaction rate constant (from literature) = k = 3.32×10^{-5} 1/s

Input Parameters

The input parameters required for the determination of the external mass transfer coefficient were as follows:

1. Initial substrate concentration
2. Final substrate concentration
3. Final Bio film thickness
4. Final Biomass concentration
5. Bed porosity

Biofilm Thickness Determination

The biofilm thickness was determined through SEM analysis of bio-particles before and after operation in the fluidized bed reactor. The increase in biomass concentration on the supporting media during reactor operation leads to an increase in the volume of bio-particles.

Biofilm Dry Density Calculation

After determining the biofilm thickness, the biofilm dry density (ρ) was calculated using the empirical relation proposed by Rui A. Boaventura and A. E. Rodrigues:

$\rho = 104.3 - 0.1245l$ (l in μm) .....(1)

Bed Porosity Determination

Bed porosity (ε) was defined as the ratio of the void volume to the total volume of the bed. The void volume was calculated by the difference between the total volume and the total volume of all bio-particles.

$$\varepsilon = 1 - \frac{Vs}{Ah_f} \quad \text{.....(2)}$$

Where Vs is the total volume of bio-particles, A is the area of the cross-section of the bed, and hf is the height of the expanded bed.

Observed Reaction Rate

The observed reaction rate (Robs), representing the substrate removal rate, was calculated using the initial and final concentrations of the substrate and the operation time of the fluidized bed reactor:

$$R_{obs} = \frac{(S_f - S_b)}{T} \quad \text{.....(3)}$$

Biofilm Volume/Biofilm Exterior Surface Area

For spherical bio-particles, the biofilm volume to biofilm exterior surface area ratio (r) was calculated to eliminate geometric differences.

$$r = \frac{biofilm\ volume}{biofilm\ exterior\ surface\ area}$$

$$\bar{r} = \frac{\frac{4}{3}\pi\left(r_p^3 - r_m^3\right)}{4\pi \cdot r_p^2} \quad \text{.....(4)}$$

Thiele Modulus

A modified zero-order Thiele modulus (ϕ) was defined as:

$$\phi_{om} = \bar{r}\left(\frac{\rho k_o}{DS_b}\right)^{0.5} \quad \text{.....(5)}$$

Effectiveness Factor

An explicit relationship between the effectiveness factor (η) and the modified Thiele modulus (ϕ) was obtained:

$$\eta = 0.132\phi_{om}^{-0.9} \quad \text{.....(6)}$$

Observed Reaction Rate as Predicted by Model

The observed reaction rate per unit fluidized bed volume (Robs,model) for the zero-order reaction in the partially penetrated bio-particles was expressed as the product of the observed rate per unit biofilm mass (R) and the biofilm mass per unit fluidized bed volume (X).

$R_{obs,model} = \eta k_0 X$ .....(7)

External Mass Transfer Coefficient

The external mass transfer coefficient (KL) was calculated using the equation relating the substrate consumption rate in the fluidized bed to the overall external mass transfer rate

$$KL = \frac{Robs,model\ V}{Apnp(Sb - Ss)} \quad \text{.....(8)}$$

Where V is the void volume of the reactor, A is the cross-sectional area of the reactor, p is the porosity of the bed, and (Sb−Ss) is the difference between the bulk substrate concentration and the substrate concentration at the biofilm surface.

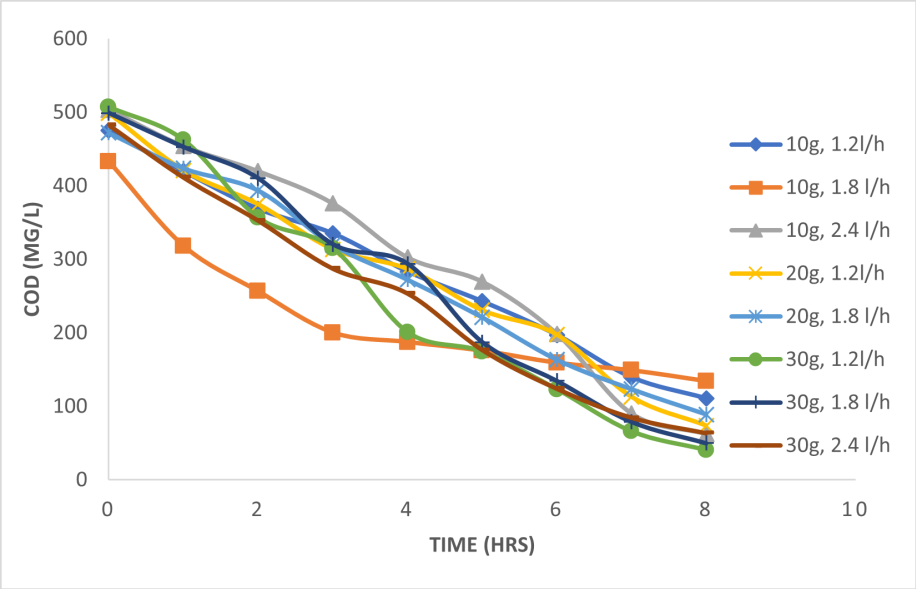
The void volume (V) was related to the total volume of the reactor (V0) as V=V0ε.

RESULTS AND DISCUSSION

Impact of Initial Granular Activated Carbon Mass and Flow Rate on COD Reduction in an 8- Hour Treatment Process

The study investigated the impact of initial granular activated carbon (GAC) mass (10g, 20g, 30g) and flow rate (1.2 l/h, 1.8 l/h, 2.4 l/h) on Chemical Oxygen Demand (COD) reduction over an 8-hour period. Results indicated that higher flow rates, particularly 2.4 l/h, accelerated COD removal. The most substantial COD decrease (from 507.21 mg/L to 40.32 mg/L) occurred at a GAC loading of 30g and a flow rate of 1.2 l/h. Although increasing GAC mass correlated with higher initial COD levels, effective reduction was contingent on optimized flow rates.

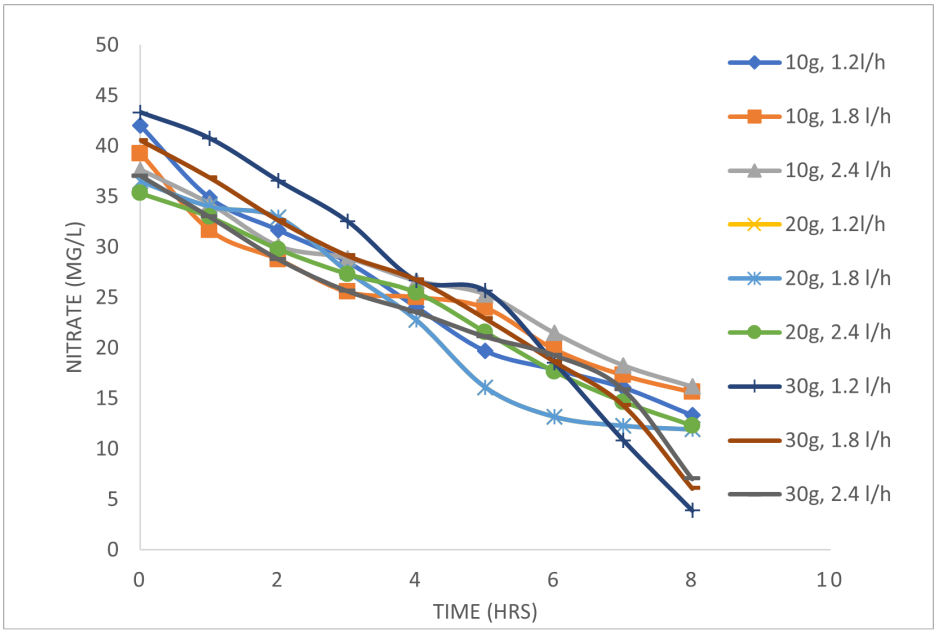
Figure 2. COD reduction over time with varying GAC masses and flow rates.



Impact of granular activated carbon mass and flow rate on nitrate removal efficiency over time

The study examined nitrate removal over 8 hours using different initial masses of granular activated carbon (10g, 20g, 30g) and flow rates (1.2 l/h, 1.8 l/h, 2.4 l/h). Results showed that lower flow rates (1.2 l/h) were more effective in removing nitrates due to increased contact time, with the most significant reduction observed for 10g at 1.2 l/h (from 42.01 mg/L to 13.35 mg/L). Higher initial masses achieved higher initial removal rates but saw faster declines in efficiency.

Figure 3. Nitrate removal efficiency over time with varying GAC masses and flow rates,



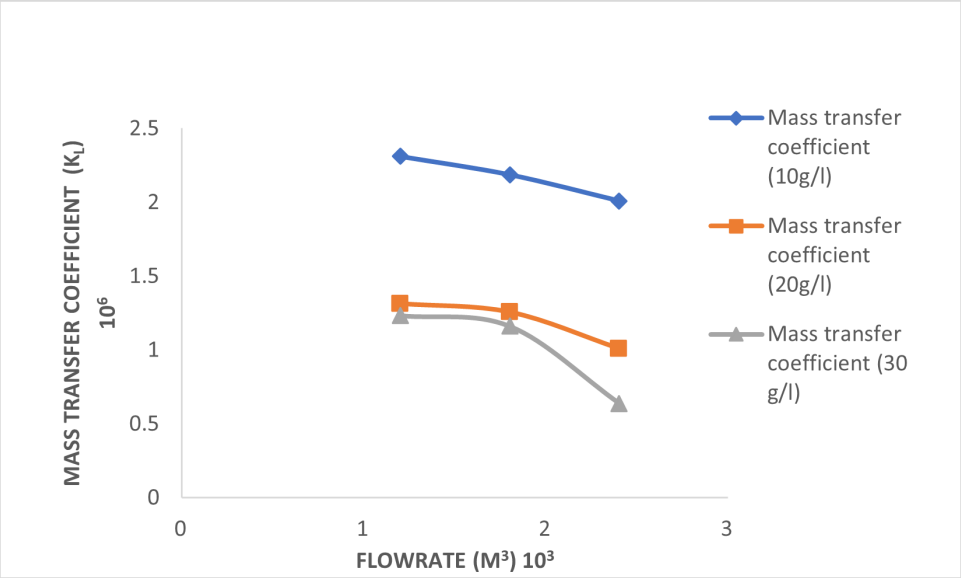
SEM analysis and impact of biofilm thickness variability on behavior and predictive modelling

Biofilm thickness was determined by SEM analysis of bioparticles before and after running in the reactor. SEM micrographs revealed a heterogeneous biofilm structure with thickness ranging from 3.22 to 7.02 µm. This variability significantly impacts biofilm behavior, influencing factors such as mass transfer, nutrient diffusion, and antimicrobial resistance. The quantitative data obtained from these images served as the foundation for a mathematical model developed to predict biofilm growth, responses to environmental changes, and treatment efficacy. Understanding this complex structure is crucial for developing effective strategies to control biofilm formation and persistence in spouted bed reactors.

Variation of Mass Transfer Coefficient with Flow Rate and GAC Loading: Model-Based Insights

The mass transfer coefficient decreased as flow rate increased across all GAC loadings. Higher GAC loadings resulted in lower mass transfer coefficient values, likely due to increased biofilm thickness hindering mass transfer. Conversely, lower GAC loadings exhibited better mass transfer efficiency, suggesting that optimal system performance requires careful consideration of both GAC loading and flow rate.

Figure 4. Variation of Mass Transfer Coefficient with Flow Rate and GAC Loading: Model-Based Insights.



CONCLUSION

In conclusion, this study provides critical insights into the performance of spouted bed reactors (SBRs) for nitrate and chemical oxygen demand (COD) reduction from industrial wastewater under aerobic conditions. The results indicate that higher flow rates (2.4 l/h) enhance COD removal, with the most effective reduction observed at 30g of granular activated carbon (GAC) and a flow rate of 1.2 l/h. For nitrate removal, lower flow rates (1.2 l/h) proved more effective, with optimal performance achieved with 10g of GAC. Scanning Electron Microscopy (SEM) analysis revealed heterogeneous biofilm structures with thicknesses ranging from 3.22 to 7.02 µm, significantly influencing biofilm behavior and mass transfer. The study also identified that the mass transfer coefficient decreases with increasing flow rates and GAC loading, highlighting the need for careful optimization of these parameters. The developed mathematical model, based on SEM data, offers valuable predictions for biofilm growth and reactor performance. These findings contribute to refining SBR technology for wastewater treatment, emphasizing the importance of balancing operational parameters to maximize treatment efficiency and sustainability.

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