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Trickle Bed Biodesulfurizer of Diesel with Backwash and Recycle

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Production of ultra low sulfur diesel through biodesulfurization process has been studied in a trickle bed reactor having a diameter of 0.066 m and a height of 0.6 m. Rhodococcus sp.(no. 2891 NCIM, Pune) in immobilized form has been used to desulfurize hydrotreated diesel having sulfur concentration in the range of 200–540 ppm. The initial substrate concentration, recycle ratio and volumetric flow rate have been chosen as process parameters. Excess biomass accumulation, which is reflected by the increment of pressure drop within the reactor, has been avoided by backwashing technique. Backwashing time has been correlated to volumetric flow rate. A deterministic mathematical model based on the growth kinetic parameters, namely, maximum specific growth rate μ_{max}, *saturation constant* K_s *and yield coefficient* $Y_{A/B}$, *determined using systematic batch studies has been developed. Simulated data have been compared with the experimental results, which signify that the model predictions can explain the reality satisfactorily.* © 2007 American Institute of Chemical Engineers *AIChE J*, 53: 2188–2197, 2007

Keywords: bio-desulfurization of diesel, trickle bed reactor, immobilized microorganisms, mathematical modeling

Introduction

Acid rain caused by the emission of sulfur oxides during the combustion of petroleum fraction, particularly diesel containing an array of organo-sulfur compounds like benzothiophene (BT), dibenzothiophene (DBT), and alkylated DBTs, is of great environmental concern. Catalytic hydrodesulfurization of diesel in trickle bed reactors using severe operating condition (Pressure 20–80 bar; Temperature = 320–380°C) and CoMo/NiMo[1,2] catalysts is the most popular process followed by the refiners for the removal of organo-sulfur compounds. However, this process cannot completely remove the recalcitrant compounds like DBT and alkylated DBTs. As a consequence even after hydrotreatment, diesel stream contains alkylated family of DBTs and DBT itself and the sulfur level of hydrotreated diesel does not go down below 100 mg/dm^3 even after using stringent operating condition, namely very high temperature and hydrogen pressure.[3] In contrary, US, Japan, and Western Europe have been implementing regulations which will enforce the refiners to produce "Near Zero Sulfur Diesel"[4] (sulfur concentration of 15 mg/dm^3 or less) to ensure clean environment. Therefore, the refiners, all over the world and particularly in western countries, are under pressure to search for a suitable sulfur-removal process of diesel either as an alternative to hydrodesulfurization or as a complementary process to serve as the successor of hydrodesulfurization step.[5,6] As the hydrodesulfurization has already gained popularity due to its efficiency in removing organo-sulfur compounds other than DBTs, it is always advisable to explore the possibility of using an efficient process, which can lower down the sulfur level in hydrotreated diesel to an ultra-low value. From this perspective biodesulfurization may serve as a potential route for the removal of refractory organo-sulfur compounds of DBT family remaining unconverted after the hydrodesulfurization of diesel.[7] Bio-desulphurization is a process that removes sulfur

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Table 1. Characteristics of Hydrotreated Diesel Sample

Compound	IBP, °C	FBP, °C	Sp. Gravity (Basis:density of water = 1000 kg/m^3)	Density, kg/m^3	Viscosity, Kg/m^3/s	Sulfur, ppm	Aromatic, % (w/w)
Diesel	140	370	0.8216	832.4	0.002081	200–540	27.16

from fossil fuels using a series of enzyme-catalyzed reactions and the final product is a hydrotrope and may be used as a surfactant.[7] Although several articles[5,6,8–11] have been reported in this area, most of them concentrate on the exploration of new microorganisms for desulfurization of diesel. Main objective of many of them is the determination of growth kinetics of the newly explored microorganisms[6,8–11] based on batch type experimental works. Only a few groups[12–15] have reported on the performance of the real reactors. However, even in these articles thrust has been given on the operation of conventional bioreactors of CSTR type where a mixture of aqueous phase and diesel has been treated with suitable microorganisms. Biodesulfurization in chemostats is, however, characterized with the problem of separation of diesel phase from the aqueous one containing microorganisms demanding a thorough down-stream processing. From that perspective use of microorganisms in immobilized form is however beneficial as this does not require further treatment process for the separation of diesel from aqueous phase. Further, it ensures the availability of microorganisms for several treatment runs. Thus the treatment of hydrodesulfurized diesel in a trickle bed reactor containing packing for immobilization of microorganisms may be more attractive to the refiners. Under the present investigation, a trickle bed reactor packed with pith balls holding the biofilms of desulfurizing bacteria *Rhodococcus* sp., undergoing sulfur degradation through 4S pathway has been used. Instead of using mixture of aqueous and nonaqueous phases, only diesel was flown through the reactor to avoid the problem of subsequent oil–water separation. Inlet sulfur concentration, volumetric flow rate, and recycle ratio have been used as parameters. A concept of "back wash time"—operating time after which the regeneration of trickling bio reactor is required to avoid clogging has been introduced. From the literature review it appears that although mathematical models for the hydrodesulfurizing trickle bed reactors are abundant,[1,14,15] mathematical analysis of biotrickling reactors undergoing ultra desulfurization of diesel is rare.[16–19] Under the present investigation, a two-phase unstructured mathematical model has been developed for the biotrickling reactor incorporating the effect of recycle into account. Transient changes in bed porosity and pressure drop have been analyzed from the perspective of smooth operation of the reactor. Apart from the analysis of axial profile of sulfur in the diesel stream, its radial distribution along the biofilm has also been analyzed using a suitable model.

Experimental

Materials

Beef extract (E. Merck), Peptone (E. Merck), NaCl (Ranbaxy), Methanol (E. Merck), Acetone (E. Merck), Benzothiophene (Lancester), N_2 (Prakash traders), Dithiozone (E. Merck), NaOH (E. Merck), Acetic acid (Process chemical industries), Mercuric oxide (E. Merck), HCl (E.Merck), Isopropyl alcohol (Process chemical industries), Nickel aluminum alloy (E. Merck), and Hexadecane (E. Merck) were used during the present investigation.

Microorganism. The pure bacterial strain of *Rhodococcus* sp. (NCIM. 2891) was purchased from NCIM (National Collection of Industrial Microorganisms), India. Cells were cultivated and were enriched using sulfur free medium supplemented with diesel oil in 50-ml Erlenmeyer flasks. *Rhodococcus* sp. used during the present investigation can grow in the oil phase only. This has been tested by growing the culture in 100% diesel.

Diesel Used. Hydrodesulfurized diesel samples were purchased from IOC (Indian Oil Corporation, Kolkata) having the characteristics given in Table 1.

Composition of the Growth Medium for Microorganisms (Basis 1 dm^3). Beef extract, 10 g; NaCl (AR), 5 g; Peptone (for bacteriology), 10 g.

Packing Material. Pith balls which are a kind of "ground tissue" in the center of the stem or root. It consists primarily of parenchyma, a sort of thin-walled cell in plant, with lignified secondary wall. This is an inert material. Because of the presence of lignin it is not acted upon by microorganisms. The density of the material is 540 kg/m^3.

Analytical methods

Dry weight Method for the determination of Bacterial Mass: The biomass concentration in the reaction broth was determined by dry weight method.[20] In this method the broth was centrifuged at the rate of 10,000 rpm for 15 min at −15°C. The bacterial mass was then transferred to a preweighed aluminum cup and dried at 50°C overnight. The exact weight of the bacterial mass was determined by subtracting the weight of dry cup from that of the cup containing dry bacterial mass.

Sulfur Analysis. UOP 357-80 (Trace Sulfur in Petroleum Distillates by Nickel Reduction) method has been followed to determine the concentration of sulfur in the diesel samples.

Batch experiments for the determination of kinetic parameters

Batch type experiments were conducted in Erlenmeyer flasks. The overall sulfur concentration was varied from 200 to 540 mg/dm^3. The concentration time histories of biomass and substrate were analyzed and were observed to follow the trend of classical Monod type kinetics. The kinetic parameters like μ_{max} and K_s and $Y_{A/B}$ were determined by the nonlinear analysis of these data and are represented in Table 2.

Table 2. Values of Growth Kinetic Parameters and Diffusivity of Diesel Sulfur in Biofilm

Saturation Constant, K_s, mg/dm^3	Maximum Specific Growth Rate, μ_{max}, h^{-1}	Yield Coefficient, $Y_{A/B}$	Diffusivity of Diesel Sulfur Concentration in Biofilm, D_{AB}, m^3/s
71	0.0961	0.2	3.58×10^{-10}

Description of the trickle bed reactor

The reactor has a diameter of 6.6 cm and a height of 60 cm. The reactor is connected to a sterile diesel reservoir by sterilized pipes through which diesel flows into the reactor by means of a peristaltic pump. The reactor outlet at the bottom is bifurcated so that one stream is recycled and the other stream is taken out as the net product. Two rotameters are used to control and measure the inlet and outlet rates. Diesel enters into the reactor from the top, trickles down and comes out from the bottom of the reactor. Air is continuously sparged into the reactor from the bottom counter currently with the diesel stream and comes out from the top of the reactor. Another rotameter is used to control and measure the inlet air flow rate.

Operation of the trickle bed bio-reactor

The experiment was carried out in the trickle bed reactor in continuous mode. Hydro-treated diesel was used as sulfur source. The reactor was initially packed with pith balls of 12 mm diameters. Microorganisms were immobilized on the UV sterilized packing material by continuous recirculation of the bacterial medium containing *Rhodococcus* sp. having the biomass concentration of 20 g/dm^3 through the packed bed until the bio-film thickness on the packing was determined to be 0.1 mm. The entire immobilization process was done in a sterile condition in the environment of an alcohol flame. The reactor was equipped with an air compressor for continuous aeration of the system to facilitate the growth of the aerobic bacteria. The reactor was run under atmospheric pressure. The initial bed voidage was 0.6. During the course of reaction, the biofilm thickness over the packing sphere increased because of bacterial growth. This led to a decrease in bed voidage resulting in increase in pressure drop. The voidage of the bed was measured at different intervals by interrupting the experiment. Pressure drop was continuously measured during the experiment. When the pressure drop reached 60% of the operating pressure, backwashing was performed to avoid clogging of the reactor bed. All the pipelines were made sterile before the commencement of each experiment. The reactor was continuously sparged with air at 480 dm^3/h in upward direction. Diesel having different organo-sulfur concentration namely, 200, 330, 430, and 540 mg/dm^3 was fed into the trickle bed reactor at a rate varying from 0.25 to 0.5 dm^3/h (LPH) in downward direction. The recycle ratio was varied in the range of 0.25–0.75 to ensure high conversion of sulfur. The reactor residence time varied from 4 to 8 h. Steady state with respect to diesel sulfur was observed to be attained after an operating time period of one residence time, $\tau = V/v_{net}$. Effluent stream of the bio-reactor was analyzed for biomass using dry weight method and for organo-sulfur compounds using Nickel reduction method (UOP357-80) and X-ray fluorescence method, respectively.

Measurement of pressure drop through the reactor bed

Pressure drop within the reactor was measured using U-tube manometer.

Measurement of reactor voidage

At the moment of measurement of voidage of the reactor bed, all residual liquid inside the reactor was allowed to flow down so that the packing became free from any liquid component. Subsequently the packings were made dry by the passage of air. Fresh diesel was then introduced into the bed to fill up the void space. Void volume was calculated from the quantity of diesel to be added to fill the packed bed. Bed voidage was evaluated by taking the ratio between void volume and the total volume of the packed bed.

Theoretical analysis

The trickle bed bio-reactor has been schematically represented in Figure 1a. General arrangement of packings in the reactor has been shown in Figure 1b and 1c. The mathematical model of the system has been developed on the basis of the following assumptions,

1. Influent stream of the bio-reactor is sterile.
2. Organo-sulfur compounds are the only growth limiting sulfur source.
3. Microbial reaction occurs only at the outer surface of the bio-film.
4. There is no external mass transfer resistance present in the system. As it has been observed that the conversion has a linear relationship with particle size it is assumed that the chemical reaction is the controlling step and hence the external mass transfer resistance has been neglected.
5. Microbial growth follows the Monod kinetics.
6. The pith balls used as immobilization matrix are perfect spheres (radius R). Some of the spheres, n, are always in contact with one spherical particle leading to loss in biofilm surface area (A_L) and volume (V_L) per unit sphere (Figure 1c) in contact.
7. As the flow regime is laminar, Kozeny–Carman equation is valid within the reactor.
8. Additional biomass produced due to biochemical reaction at the packing surface get adhered to the biofilm (Figure 1b) on packing itself and is not transported with the liquid stream.
9. Biomass concentration in the biofilm does not change, while biofilm thickness changes.
10. No biochemical reaction occurs in the recycle stream.

The system equation based on differential material balance for the organosulfur compounds of diesel is as follows:

$$\frac{dC_B}{dZ} = -\frac{1}{F_A(1+R_e)}\frac{C_B C_{A0}}{(K_s + C_B)Y}\mu_{max} \times \frac{\left[4\pi(d/2+L_f)^2 - nA_L\right]}{\frac{4}{3}\pi(d/2)^3}(1-\varepsilon)AL_f \quad (1)$$

where,

$$A_L = 2\pi[(d/2) + L_f]L_f \tag{2}$$

The biofilm thickness varies with time due to both the growth and decay of the microbial strain. This may be represented according to Alsono et al.[21] as follows,

$$\frac{dL_f}{dt}C_{A0} = \eta\frac{\mu_{max}C_B C_{A0}}{(K_s + C_B)}L_f - b_d C_{A0} L_f \tag{3}$$

Because of the change in biofilm thickness porosity of the reactor bed varies. According to Alsono et al.'s[21] concept this may be represented by the following equation,

$$\varepsilon_f = 1 - \frac{{}^4{}_3\pi(R + L_f)^3 - nV_L}{4/3\pi R^3}(1 - \varepsilon_0) \tag{4}$$

where ε_0 is Bed voidage at the start-up moment and

$$V_L = 4/3L_f^2(2L_f + 3R)$$

$$\varepsilon_f = 1 - (1 - \varepsilon_0)\left[\left(1 + \frac{L_f}{d/2}\right)^3 - \frac{n}{4}\left(\frac{L_f}{d/2}\right)^2\left(\frac{2L_f}{d/2} + 3\right)\right] \tag{4a}$$

The initial biomass density in the reactor may be represented as follows,

$$X_{b0} = C_{A0}\frac{n}{V}\left[\frac{4}{3}\pi\left(d/2 + L_f\right)^3 - \frac{4}{3}\pi\left(d/2\right)^3\right] \tag{5}$$

Although the biomass density in the biofilm is assumed to be constant, the overall density of biomass in the reactor changes. Since the additional quantity of biomass generated at any instant is $C_{A0}V(\varepsilon_0 - \varepsilon_f)$, density of biomass ($X_b$) in the bed may be correlated to its counterpart (X_{b0}) at the initial moment as follows,

$$X_b V - X_{b0} V = C_{A0} V(\varepsilon_0 - \varepsilon_f) \tag{6}$$

On elimination of V on both sides, Eq. 6 reduces to

$$X_b = X_{b0} + C_{A0}(\varepsilon_0 - \varepsilon_f) \tag{6a}$$

The radial substrate concentration profile along the biofilm thickness (L_f) surrounding each packing sphere has been shown in Figure 2. The differential mass balance equation of diesel sulfur along the radial direction in the biofilm is as follows,

$$D\left(\frac{d^2C_{BL}}{dr^2} + \frac{2}{r}\frac{dC_{BL}}{dr}\right) = \frac{\mu_{max}C_{BL}C_{A0}}{Y(K_s + C_{BL})} \tag{7}$$

The following dimensionless parameters have been introduced to make the equations dimensionless.

On introduction of dimensionless quantities, namely, C_{A0}*, C_B*, Z*, Ks*, f, t*, V*, X_{b0}* Eqs. 1 and 3–5 reduce to following Eqs. 8–11, respectively

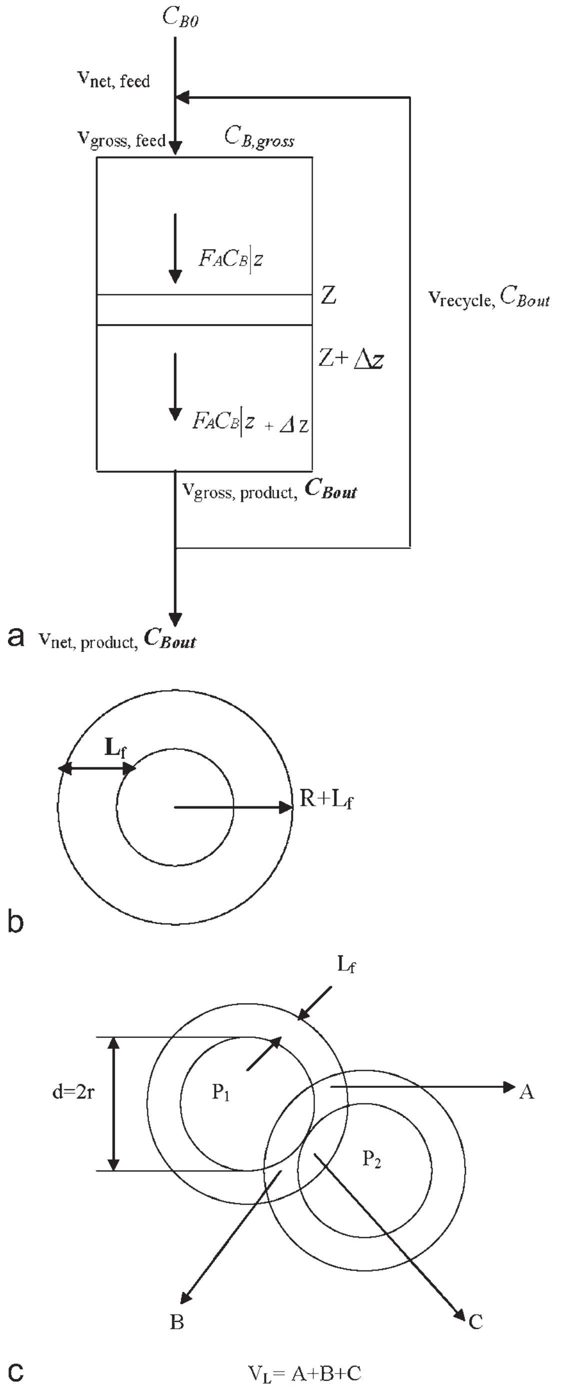

Figure 1. (a) Schematic representation of the trickle bed bioreactor and the packing materials; (b) Characteristic sphere; (c) Contacting pattern of the spheres.

F_A, Volumetric flow rate of the liquid stream; C_B, Substrate concentration; Z, axial position within the reactor. R, Radius of each packing sphere; L_f, Bio-film thickness over each packing material; A_L, Bio-film area loss per unit packing sphere in contact; V_L, Bio-film volume loss per unit packing sphere in contact.

$$\frac{dC_B^*}{dZ^*} = -B\frac{C_{A0}^*C_B^*}{K_S^*+C_B^*}\left[\frac{3f\left\{4\left(f+\frac{1}{2}\right)^2-nl\right\}}{(1/2+f)^3}\right](1-\varepsilon)f \qquad (8)$$

where,

$$B = \frac{1}{(1+R)}\frac{1}{Y}\mu_{\max}\tau$$

and

$$l = 2\pi f(1/2+f)$$

$C_B^* = \frac{C_B}{C_{B0}}$, $C_{A0}^* = \frac{C_{A0}}{C_{B0}}$, $Z^* = \frac{Z}{L}$, $Ks^* = \frac{Ks}{C_{B0}}$, $f = \frac{L_f}{d}$, $r^* = \frac{r}{R}$, $V^* = \frac{V}{(\pi d^3/6)}$, and $Xb_0^* = \frac{X_{b0}}{C_B}$

$$\frac{df}{dt^*} = f\left[\frac{\tau\mu_{\max}C_B^*}{Ks^*+C_B^*} - b_d\tau\right] \qquad (9)$$

$$\varepsilon_f = 1-(1-\varepsilon_0)\left[(1+2f)^3 - nf^2(4f+3)\right] \qquad (10)$$

$$X_{b0}^* = \frac{n}{V^*}C_{A0}^*\left[(1+2f)^3-1\right] \qquad (11)$$

The boundary conditions are as follows,

For $t^* \le 0, Z^* = 0$

$$\left|\begin{array}{c} C_A{}^* = C_{A0}{}^* = \text{constant} \\ C_B{}^* = C_{B0}{}^* \\ f = f_0 \\ \varepsilon = \varepsilon_0 \end{array}\right|$$

for $t^* > 0, Z^* = 0$

$$\left|\begin{array}{c} C_A{}^* = C_{A0}{}^* = \text{constant} \\ C_B{}^* = C_{\text{Bgross}} = \dfrac{C_{B0}{}^* + RC_{\text{Bout}}{}^*}{(1+R)}(t^*, Z^*=1) \\ f = f(t^*) \\ \varepsilon = \varepsilon_f(t^*) \end{array}\right|$$

Introducing the dimensionless quantity, namely, r^* and P, the Eq. 7 acquires the following dimensionless form,

$$D\left(\frac{d^2C_{BL}^*}{dr^{2^*}} + \frac{2}{r^*}\frac{dC_{BL}^*}{dr^*}\right) = \frac{\mu_{\max}C_{BL}^*C_A^*R^2}{Y(Ks^*+C_{BL}^*)} \qquad (12)$$

where, $r^* = \frac{r}{R}$

Applying L' Hospital's correction,[22]

$$\frac{1}{r}\frac{dC_{BL}^*}{dr^*} = \frac{d^2C_{BL}^*}{dr^{2^*}}$$

Then Eq. 12 becomes,

$$3\frac{d^2C_{BL}^*}{dr^{2^*}} = \frac{\mu_{\max}C_{BL}^{2*}C_A^*R^2}{YD(Ks^*+C_{BL}^*C_{B0})} \qquad (13)$$

$$\frac{d^2C_{BL}^*}{dr^{2^*}} = \frac{PC_{BL}^{2*}C_A^*}{(Ks^*+C_{BL}^*C_{B0})} \qquad (13a)$$

where, $P = \frac{\mu_{\max}R^2}{3YD}$

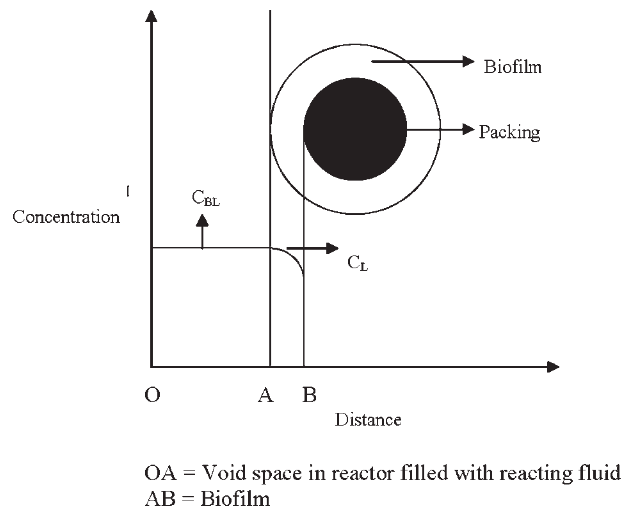

Figure 2. Schematic representation of concentration profile of sulfur compounds in biofilm and the adjacent layers.

The boundary condition is as follows,

At $r^* = 1$, $\frac{dC_{BL}^*}{dr^*} = 0$ and at $r^* = \frac{R+L_f}{R} = 1+2f$, $C_{BL}^* = C_B^*$ (Since $C_{BL} = C_B$)

Pressure drop over the bed has been calculated using Kozeny–Carman equation as follows,

$$\Delta P = \Delta Z\left[\frac{150V_0\pi}{\phi^2 d^2}\frac{(1-\varepsilon_f)^2}{\varepsilon_f{}^3}\right] \qquad (14)$$

The Eqs. 1–6a, 8–11, and 14 have been solved using 4th order Runge–Kutta technique with the aid of a suitable C-program. The growth kinetic parameters, maximum specific growth rate $\mu_{\max}$, and saturation constant K_s have been determined by nonlinear analysis of the experimental data obtained from experiments conducted in batch mode. Equation 7 and hence Eqs. 12–13a have been solved by the method of central finite difference technique and the corresponding matrix equation have been solved numerically by Gauss Jordon elimination method[22] with the aid of suitable C-programs.

Results and Discussion

Characterization of microbial kinetics

The growth kinetics of *Rhodococcus* sp. as determined from classical Monod model include the values of $\mu_{\max}$, K_s, and $Y_{A/B}$ and are reported in Table 2.

Reactor performance

Effects of different parameters like initial substrate concentration, inlet diesel flow rate, and recycle ratio on the reactor performance have been studied experimentally and through mathematical modeling. Sulfur concentration in diesel and bed voidage have been chosen as two important dependent parameters of the reactor.

Pattern of dependence of sulfur concentration along reactor length

Axial profile of sulfur concentration in diesel along the reactor is dependent on all the independent operating parameters, namely, sulfur concentration in inlet diesel, volumetric flow rate, and recycle ratio. Effect of each independent parameter on the axial concentration of sulfur in diesel has been analyzed separately.

Effect of sulfur concentration in inlet diesel

In Figure 3 the simulated axial profiles of sulfur concentration in the diesel stream at a volumetric flow rate of 0.25 dm^3/h and recycle ratio of 0.25 has been plotted using initial sulfur concentration as a parameter. The experimental values have been superimposed on the same plot. As expected, the sulfur concentration in the diesel stream decreases along the length of the reactor for each value of inlet sulfur concentration in diesel. Close observation of the figure reveals that the sulfur concentration in the effluent stream from the reactor is dependent on the inlet concentration of sulfur. Effluent concentration of sulfur shows a decreasing trend with the decrease in the value of sulfur concentration in inlet diesel stream. The simulated trend is in good agreement with the experimental one. The value of sulfur concentration becomes almost zero in the effluent diesel stream when the inlet diesel concentration is maintained at 200 ppm. Thus normally hydrotreated diesel may easily be used to produce near zero sulfur diesels using this method of biodesulfurization.

Effect of volumetric flow rate

Figure 4 represents the simulated and experimental trends of dependence of axial profile of sulfur concentration in diesel stream when volumetric flow rate of inlet diesel is used as a parameter, keeping the values of inlet sulfur concentration at 200 ppm and recycle ratio of 0.25, respectively. From this figure it is evident that the sulfur concentration in the effluent diesel stream increases with the increase in the volumetric flow rate of inlet diesel. In other words, the ultimate conversion of sulfur in diesel increases with the decrease in the values of volumetric flow rate of diesel. The same trend has been observed at other values of inlet sulfur concentration and recycle ratio (not shown). This is justified by the fact that the decrease in volumetric flow rate ensures more residence time in the reactor resulting in enhancement of efficiency of bioconversion of sulfur in diesel. The mathematical simulation can predict the experimental trend also in this case.

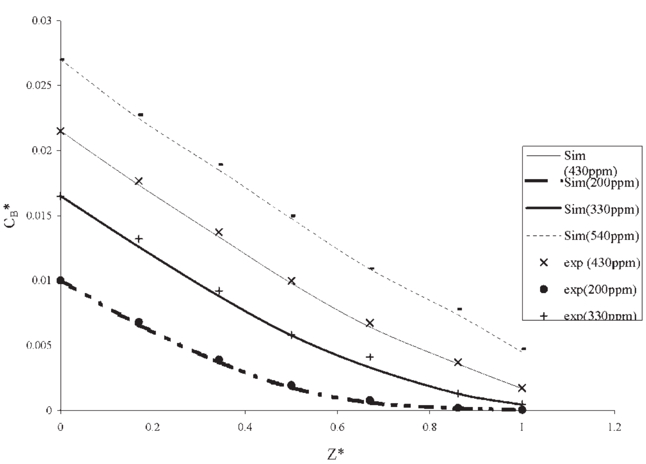

Figure 3. Simulated and experimental profiles of substrate concentration against axial length of the reactor at volumetric flow rate of 0.25 dm^3/h and recycle ratio 0.25 using initial substrate concentration as a parameter.

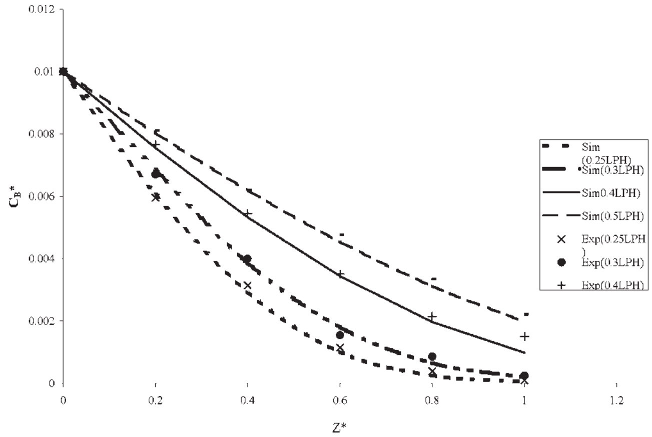

Figure 4. Simulated and experimental profiles of substrate concentration against axial length with volumetric flow rate as a parameter with initial substrate concentration 200 $mg/dm^3$and recycle ratio of 0.25.

Effect of recycle ratio

In Figure 5 theoretical and experimental dependence of axial concentration of diesel sulfur on recycle ratio (0.25–1.25) at inlet sulfur concentration of 200 ppm and net volumetric flow rate of 0.5 dm^3/h has been represented. The figure shows that the sulfur level in the effluent diesel stream decreases with the increase in the value of recycle ratio. In usual cases of chemical reactors, the trend is just the reverse, i.e., the outlet concentration of the reactant increases with the increase in the recycle ratio causing the reactor efficiency to follow a declining trend. However, the peculiar behavior of enhancement of reactor conversion efficiency with the increase in recycle ratio, as observed in the present case, is expected for autocatalytic reactions.[23] As the system under study follows autocatalytic reaction mechanism with microorganisms participating both as a reactant and a product, the trend observed from Figure 5 is quite expected. Here also the simulated trend of observation approaches the real one closely. For industrial operation of this type of biodesulfurizer for diesel, the enhancement of recycle ratio will, therefore, be beneficial to achieve higher conversion of organosulfur compounds in diesel for a certain set of values of other operation parameters.

Radial profile of sulfur concentration along the biofilm

Theoretical analysis of the radial profile of concentration of diesel sulfur along the biofilm at a representative axial position of $Z = 0.3$ m has been done using steady state mass transfer equation applicable for spherical coordinates. In Figure 6 the radial profile along the biofilm has been shown for

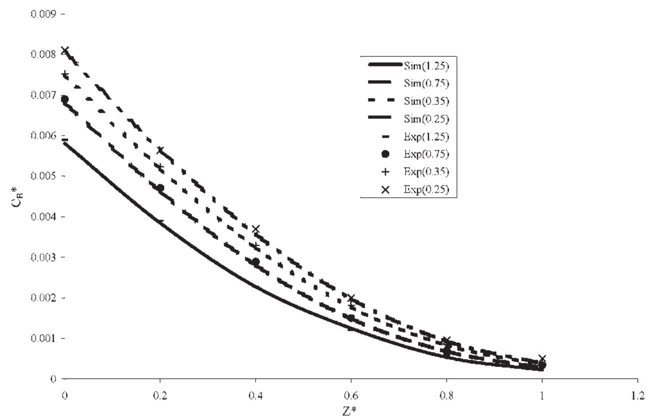

Figure 5. Simulated and experimental profiles of substrate concentration against axial length with recycle ratio as a parameter with initial substrate concentration 200 mg/dm^3 and inlet volumetric flow rate 0.5 dm^3/h.

inlet diesel sulfur concentration of 200 ppm, volumetric flow rate of 0.25 dm^3/h and recycle ratio of 1. From the close observation of the figure it is apparent that the radial concentration profile follows a declining trend towards the centre of the spherical packing with the maximum concentration prevailing at the biofilm surface.

Time histories of bed voidage and pressure drop

As the reaction operating time increases, there is a gradual increase of biomass, appearing as biofilm, in the reactor causing the voidage in the reactor bed to decrease. This, in turn, results in the increase of pressure drop over the reactor causing difficulty in its operation. Therefore, effect of different parameters, namely, inlet diesel sulfur concentration and inlet volumetric flow rate on bed voidage and pressure drop are of interest from the perspective of reactor operation.

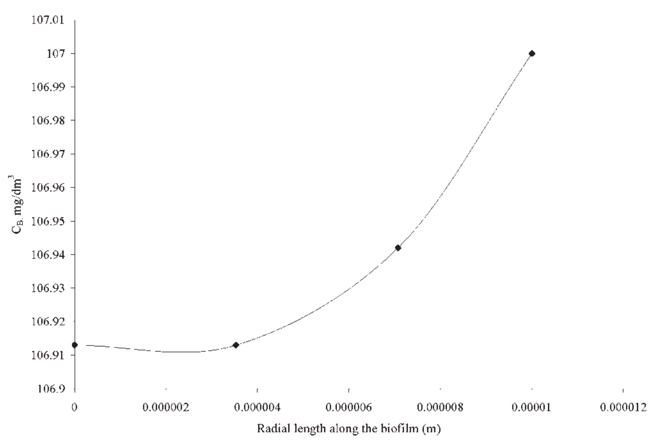

Figure 6. Simulated pattern of variation of substrate concentration along biofilm thickness at inlet sulfur concentration of 200 mg/dm^3, recycle ratio 1 and volumetric flow rate of 0.25 dm^3/h.

Effect of sulfur concentration on time history of bed voidage

Simulated values of bed voidage have been plotted against reactor operation time using inlet sulfur concentration of diesel as a parameter (200–540ppm), the values of inlet diesel flow rate and recycle ratio being set at 0.5 dm^3/h and 0.5, respectively. The experimental values obtained under the same condition have been plotted on the same figure (Figure 7). The figure reveals that for each inlet concentration of diesel sulfur the time history of voidage follows declining trend. The bed voidage decreases more sharply with time as the inlet sulfur concentration increases. This may be due to the fact that as the availability of diesel sulfur increases, the growth of microorganisms gets enhanced, and the microorganisms get attached to the packing resulting in increase of biofilm thickness and decrease of bed voidage simultaneously. The theoretical values of voidage simulated using mathematical model can explain the actual trend satisfactorily. For the inlet sulfur concentration of 540 ppm, the voidage gets reduced to zero at 18,000 s causing complete clogging of the reactor. After the propagation of this time period (= 18,000 s) the voidage becomes very low also for other inlet concentration of diesel sulfur. As this is a situation when the operation of the reactor is almost impossible without further washing, a limitation on the reaction time period is required.

Dependence of pressure drop on volumetric flow rate

The pressure drop over the reactor is closely related to its voidage. As the sharpest declining trend of time history of the bed voidage has been observed (Figure 7) for inlet sulfur concentration of 540 ppm the effect of volumetric rate on pressure drop at this value of inlet concentration has been analyzed. In Figure 8 time history of pressure drop calculated using Kozeny–Carman equation has been plotted along with the superimposition of experimental values. As expected, the pressure drop increase with the reactor operating time for

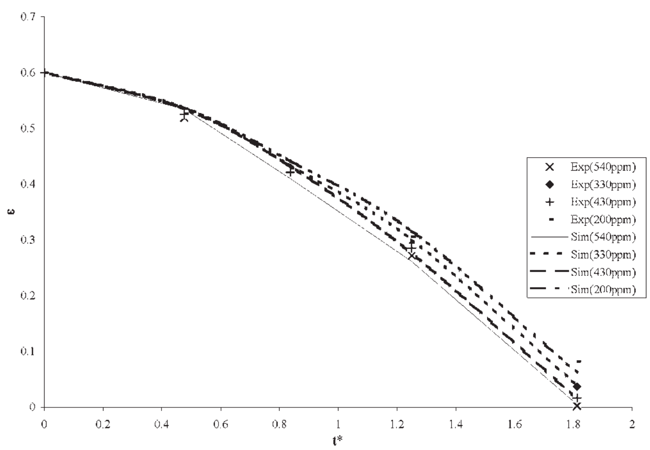

Figure 7. Simulated and experimental profiles of bed porosity against time with initial substrate concentration as parameter at volumetric flow rate of 0.5 dm^3/h and recycle ratio of 0.5.

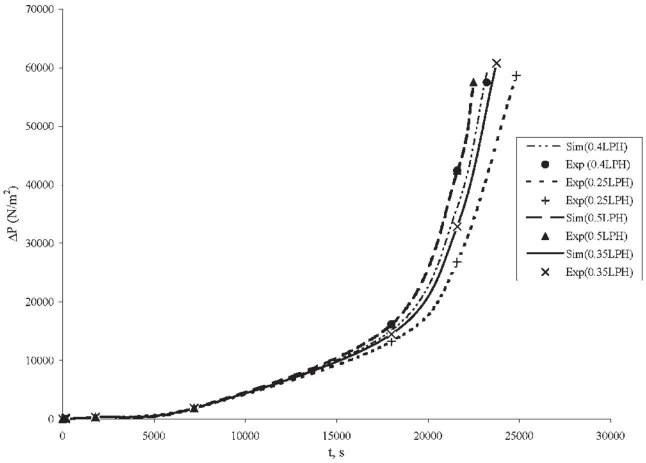

Figure 8. Simulated and experimental pressure drop profile within the reactor against time at initial sulfur concentration 540 mg/dm^3 and recycle ratio of 0.25 with inlet volumetric flow rate as a parameter.

each volumetric flow rate of inlet diesel. With the increase in the volumetric flow rate, the sharpness of increasing trend of time histories of pressure drop increases. This may be due to the linear dependence of pressure drop on volumetric flow rate.

Backwashing time—definition and significance

From the analysis of dependence of hydrodynamic parameters like pressure drop and voidage on inlet concentration of diesel sulfur and volumetric flow rate, it seems necessary to define a time period up to which the reactor may be operated without facing the clogging situation associated with the tremendous pressure drop. From this perspective, a critical time called backwashing time has been introduced which signifies the reactor operating period at which the pressure drop becomes 60% of the operating pressure of the system. Under the study, this time has been considered to be the limit after which it is mandatory to backwash the reactor for its regeneration. From the analysis of Figure 8, it has been observed that the backwashing time is dependent on the volumetric flow rate and thus a correlation ($t_{BW} = 30{,}000F_A^2 - 32{,}331F_A + 31{,}107$) between these two parameters has been sought using nonlinear regression technique. In Figure 9 the dependence of backwashing time on inlet flow rate of diesel has been shown using both simulated and experimental values. From the analysis of the figure it is understandable that the correlation can explain the experimental trend well. It is expected that this correlation will help future workers deciding on the backwashing time of biodesulfurizers of diesel based on similar microorganisms.

Time history of axial concentration of diesel sulfur

It is of interest to study the pattern of change of axial concentration profile of diesel sulfur over the reactor operating period up to a maximum value of backwashing time. For this purpose, simulated axial profiles of sulfur concentration have

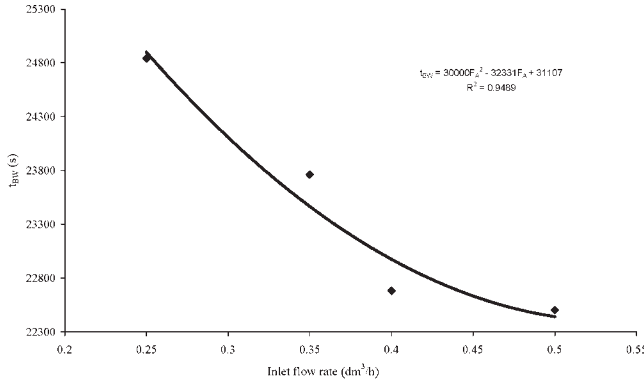

Figure 9. Dependence (Experimental: points; Regression: line) of backwashing time on inlet flow rate at Z = 0.3 m.

been plotted at different values of operating times over a span up to the backwashing time, the values of recycle ratio, inlet sulfur concentration and volumetric flow rate being set at 0.25, 200 ppm and 0.25 dm^3/h, respectively (Figure 10). The experimental values have also been plotted on the same figure. From a thorough analysis of the figure it is evident that as the time progresses the conversion efficiency obtained at different axial position increases. This is expected due to the fact that as reaction time proceeds there is more scope of sulfur degradation reaction to occur facilitating the removal of sulfur from diesel until the backwashing condition is reached. The simulated and experimental results are in good agreement also in this case.

Conclusion

The bacterial strain, namely, *Rhodococcus* sp.(NCIM 2891) used in the present study has shown high activity to reduce the sulfur level in diesel .The initial sulfur concentra-

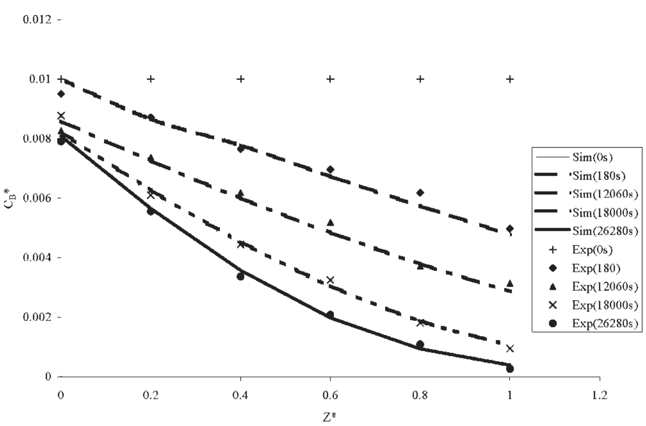

Figure 10. Simulated and experimental profiles of substrate concentration against axial length with time as a parameter at recycle ratio 0.25, initial substrate concentration 200 mg/dm^3 and inlet volumetric flow rate of 0.25 dm^3/h.

tion is varied in the range of 200–540 mg/dm^3. A trickle bed reactor has been studied with the liquid flow rate, recycle ratio, and inlet sulfur concentration as parameters. Bed voidage and pressure drop have been measured during the operation of the reactor. A mathematical model capable of describing the biodesulfurization of diesel in a trickle bed reactor has been proposed. Backwashing time—a limiting time at which the reactor pressure drop becomes equal to 60% of the initial operating pressure—has been correlated with the inlet flow rate using a nonlinear equation. The simulated values are able to explain the experimental observation satisfactorily. However, it is felt that there is a scope of refinement of the model by the incorporation of more realistic characteristics such as effects of external mass transfer resistance, liquid hold-up behavior, wettability criterion, etc. prevailing in the actual trickle bed system.

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Notation

A = Cross-sectional area of the reactor, m^2
A_L = Bio-film area loss per unit packing sphere in contact, m^2
b_d = Biomass decay rate coefficient, s^{-1}
C_A = Biomass concentration in the biofilm, mg/dm^3
C_B = Substrate concentration, mg/dm^3
C_{Gross} = Substrate concentration in combined (feed plus recycle) stream, mg/dm^3
C_{BL} = Substrate concentration in the biofilm, mg/dm^3
D = Diffusivity of diesel sulfur concentration in biofilm, m^2/s
D = Diameter of each packing sphere, m
F_A = Volumetric flow rate (= v_{gross} in Figure 1a) of the liquid stream, dm^3/h
K_s = Saturation constant
L = Length of the reactor, m
L_f = Bio-film thickness over each packing material, m
N = Number of packing spheres in contact with one sphere within the TBR, dimensionless
ΔP = Pressure drop
R = Radius of each packing sphere (pith ball), m
Re = Recycle ratio =(Recycle rate/net feed rate), dimensionless
r_A = Cell growth rate, mg/dm^3 h
$(-r_B)$ = Substrate consumption rate, mg/dm^3 h
T = Time elapsed after the starting of trickle bed reactor, s
τ = Residence time, h
t_{BW} = Backwashing time, s
V = Volume of the TBR, m^3
V_L = Bio-film volume loss per unit packing sphere in contact, m^3
v_{gross} = Gross volumetric flow rate (shown in Figure 1a), dm^3/h
v_{net} = Net volumetric flow rate (shown in Figure 1a), dm^3/h
$v_{recycle}$ = Volumetric flow rate of recycle stream (shown in Figure 1a), dm^3/h
X_{b0} = Initial biomass density in the reactor bed, mg/dm^3
X_b = Biomass density in the reactor bed at any time t, mg/dm^3
$Y_{A/B}$ = Yield coefficient (= Mass of biomass produced/mass of substrate consumed), dimensionless
Z = Axial position within the reactor, m

Greek letters

ε = Initial bed porosity
ε_f = Porosity in bed with bio-film
Φ = Sphericity of the packing materials
μ = Viscosity of the liquid (diesel), cp
μ_{max} = Maximum specific growth rate of biomass, h^{-1}
τ = Residence time, h

Abbreviations

IBP = Initial Boiling Point, °C
FBP = Final Boiling Point, °C

Subscripts

Gross = of combined stream of inlet and recycle
Max = Maximum
Out = of outlet stream
feed = of feed
product = of product
0 = of inlet stream

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