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Two phase mathematical model for a bio-trickling reactor for the production of ultra low sulfur diesel (ULSD) from deeply hydrodesulfurized diesel

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Abstract

A trickle bed reactor (TBR) having a diameter of 0.066 m and a height of 0.6 m has been used for the bio-desulfurization of hydrotreated diesel fraction having sulfur concentration in the range of 200–540 ppm. *Rhodococcus* sp. (NCIM 2891, Pune) has been used to degrade the residual organo-sulfur compounds present in deeply hydrodesulfurized diesel. The microorganisms have been immobilized on the packing material prior to desulfurization within the trickle bed reactor. The volumetric flow rate and hence, the substrate loading rate have been used as the parameters. Sulfur reduction within the range of 84–95% has been achieved. To avoid the excess accumulation of the biomass within the reactor, backwashing technique is incorporated. For such desulfurization, batch studies have been conducted in Erlenmeyer flasks maintaining the concentration of diesel in the range of 0–100% in a diesel supplemented sulfur-free aqueous medium. The concentration of biomass with time has been monitored using dry cell weight method. The concentration of sulfur has been determined by ''trace sulfur in petroleum distillate by nickel reduction'' (UOP 357-80) method. From the growth curve, it is observed that the system follows uninhibited Monod type model within the range of substrate studied. A systematic and programmed investigation has been carried out to determine the growth kinetic parameters, namely maximum specific growth rate, saturation constant K_s and yield coefficient $Y_{X/S}$. A deterministic mathematical model for the TBR has been developed using judicious assumptions to predict its performance characteristics.

Keywords: Bio-desulfurization; Uninhibited Monod model; Intrinsic kinetic parameters; Trickle bed reactor; Immobilized; Two phase mathematical model

1. Introduction

Sulfur is the most undesirable element present in petroleum fractions. Diesel contains various organo-sulfur compounds, which not only contribute to air pollution, but causes severe hazardous impact on environmental safety leading to serious damage to eco-system. Most of the major developed countries have already been compelled to legislate almost sulfur-free highway diesel fuel. In this direction, U.S. Environmental Protection Agency (EPA) has proposed a new set of fuel standards for highway diesel fuels and emissions to be phased in the beginning of 2007, according to which the new standard for fuel includes a reduction of sulfur of maximum 15 ppm. In the existing hydrodesulfurization process, using available range of catalyst (CoMo, NiMo, etc.) diverse sulfur containing compounds present in oils react in different extent and sterically hindered poly aromatic sulfur compounds, namely alkylated di-benzothiophenes, naphthothiophenes remain unconverted [1,2]. Hence, removal of sulfur to an ultra low level of 10–15 ppm is not achievable. Because of increasingly stringent regulations concerning with the sulfur content of motor fuels, sulfur removal by biocatalytic means is often considered as a potential alternative to the conventional process. Bio-desulfurization, a process in which sulfur is removed by enzymatic process, may provide a complementary technology for lowering sulfur level from 100 ppm to ultra low level of 15 ppm [8]. Microbial biocatalysts have been identified that can biotransform

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Nomenclature

A	cross-sectional area of the reactor (m)
A_L	bio-film area loss per unit packing sphere in contact (m)
b_d	biomass decay rate coefficient (s^{-1})
C_B	substrate concentration (mg/dm^3)
D_p	diameter of each packing sphere (m)
F_A	volumetric flow rate of the liquid stream (dm^3/h)
F.B.P.	final boiling point
I.B.P.	initial boiling point
K_s	saturation constant
L_f	bio-film thickness over each packing material (m)
N	number of packing spheres in contact with one sphere within the TBR
ΔP	pressure drop
R	radius of each packing sphere (pith ball) (m)
V	volume of the TBR (m^3)
V_0	average velocity of the liquid (m/s)
V_L	bio-film volume loss per unit packing sphere in contact (m^3)
X_{A0}	initial biomass concentration (mg/dm^3)
X_{b0}	initial biomass density (mg/dm^3)
X_b	final biomass density (mg/dm^3)
$Y_{X/S}$	yield coefficient = mass of biomass produced/mass of substrate consumed
Z	axial position within the reactor
Greek letters	
ε_0	initial bed porosity
ε_f	porosity in bed with bio-film
η	effectiveness factor
μ	viscosity of the liquid (diesel) (cp)
μ_{max}	maximum specific growth rate of biomass
Φ	sphericity of the packing materials
Subscript	
max	maximum

sulfur compounds that are very difficult to be removed by the conventional hydrodesulfurization. In this regard, most attention is given on Kodama 4S pathway of *Rhodococcus* sp., which can remove sulfur from substituted and unsubstituted di-benzothiophene. A few pioneering works have been reported on the bio-desulfurization of model organo-sulfur compounds [3–7,9–15]. Under the present study, bio-desulfurization has been carried out to assess the actual behaviour of natural organo-sulfur compounds occurring in diesel as the behaviour of pure model organo-sulfur compounds towards bio-desulfurization is expected to be different from that of a real system. A deterministic mathematical model, based on mechanistic approach, has been developed to simulate the system behaviour.

2. Experimental

2.1. 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) and nickel–aluminum alloy (E. Merck) were used during the present investigation.

2.2. Microorganism

The pure bacterial strain of *Rhodococcus* sp. (NCIM 2891) was purchased from National Collection of Industrial Microorganisms (NCIM), India. Cells were cultivated and enriched using sulfur-free medium supplemented with diesel oil in 50 ml Erlenmeyer flasks.

2.3. Diesel used

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

2.4. Composition of the growth medium for microorganisms

Basis: 1 dm^3, beef extract: 10 g, NaCl (AR): 5 g, peptone (for bacteriology): 10 g.

3. Analytical methods

3.1. Dry weight method for the determination of bacterial mass

The biomass concentration in the reaction broth was determined by dry weight method. 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 pre-weighed 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.

Table 1
Specification of diesel used

Compound	Diesel
I.B.P. (°C)	140
F.B.P. (°C)	370
Specific gravity (basis: density of water = 1000 kg/m^3)	0.8216
Sulfur (ppm)	200–540
Aromatic (w/w) (%)	27.16

Table 2
Values of kinetic parameters

Saturation constant, K_s (mg/dm^3)	71
Maximum specific growth rate (h^{-1})	0.0961
Yield coefficient, $Y_{X/S}$	0.2

3.2. 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.

3.3. Batch experiments for the determination of kinetic parameters

Batch type experiments were conducted in Erlenmeyer flasks. Ratio of (given in material section) aqueous medium to diesel oil was maintained in the range of 90:10 to 0:100. The overall sulfur concentration was varied from 200 to 540 ppm. The kinetic parameters like μ_{max}, K_s and $Y_{X/S}$ have been determined using these data and are represented in Table 2.

4. Operation of the trickle bed bio-reactor

The trickle bed reactor has a diameter of 0.066 m and height of 0.6 m. The reactor was initially packed with pith balls of 0.006 m diameters. Bacterial medium containing *Rhodococcus* sp., having the biomass concentration of 20,000 mg/dm^3 was circulated through the packed bed until the bio-film thickness on the sphere became 0.0001 m, which went on increasing with due course of reaction time. The initial bed porosity was 0.6, which gradually dropped down with the bacterial growth during the reaction. The reactor inlet pressure was maintained very close to atmospheric pressure. During the course of reaction, pressure drop increased following Kozeny–Carman equation. When the pressure drop reached 60% of the initial pressure, backwashing was performed. Diesel having different organo-sulfur concentration, namely 200, 330, 430 and 540 ppm 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 reactor was continuously sparged with air at 480 dm^3/h in upward direction. The substrate loading in the reactor was initially 1.46×10^{-4} kg/(m^3 h) for initial substrate concentration of 200 ppm at 0.25 dm^3/h and was varied up to 7.84×10^{-3} kg/(m^3 h) for 540 ppm of initial substrate concentration in diesel at 0.5 dm^3/h. The reactor residence time was 4–8 h. Effluent stream coming from the bio-reactor was analyzed for biomass and organo-sulfur compounds using dry weight method and nickel reduction (UOP 357-80) method, respectively.

5. Theoretical aspect: formulation of the mathematical model

The model bio-reactor has been schematically represented in Fig. 1. 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) There is no external mass transfer resistance present in the system.
(3) Organo-sulfur compounds are the only growth limiting substrates.
(4) Microbial reaction occurs only at the outer surface of the bio-film.
(5) Microbial growth follows the Monod kinetics.
(6) The immobilization matrices, namely pith balls are perfect spheres (radius R).
(7) Some of the spheres, n, are always in contact with one spherical particle and it leads to loss in bio-film surface area (A_L) and volume (V_L) per unit sphere in contact.

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

$$\frac{dC_B}{dZ} = -\frac{1}{F_A}\frac{C_B X_{A0} L_f}{(K_s + C_B)Y}\mu_{max}[4\pi(R + L_f)^2 - nA_L] \times (1 - \varepsilon_0)A \quad (1)$$

The equation for the variation of bio-film thickness due to bacterial growth on the surface of the packing material is,

$$\frac{dL_f}{dt}X_{A0} = \eta\frac{\mu_{max} C_B X_{A0}}{(K_s + C_B)}L_f - b_d X_{A0} L_f \quad (2)$$

The variation of bed porosity within the reactor is represented by,

$$\varepsilon_f = 1 - (1 - \varepsilon_0)\left[\left(1 + \frac{L_f}{R}\right)^3 - \frac{n}{4}\left(\frac{L_f}{R}\right)^2\left(\frac{2L_f}{R} + 3\right)\right] \quad (3)$$

The variation of biomass density is represented by the following equations:

$$X_b = X_{b0} + X_{A0}(\varepsilon_0 - \varepsilon_f) \quad (4)$$

$$X_{b0} = X_{A0}\frac{n}{4}\left[\frac{4}{3}\pi(R + L_f)^3 - \frac{4}{3}\pi R^3\right] \quad (5)$$

As the flow regime remained within the laminar zone, pressure drop went on increasing as the reaction proceeded, according to the Kozeny–Carman equation:

$$\Delta P = Z\left[\frac{150 V_0 \pi}{\phi D_p^2}\frac{(1 - \varepsilon_f)^2}{\varepsilon_f^3}\right] \quad (6)$$

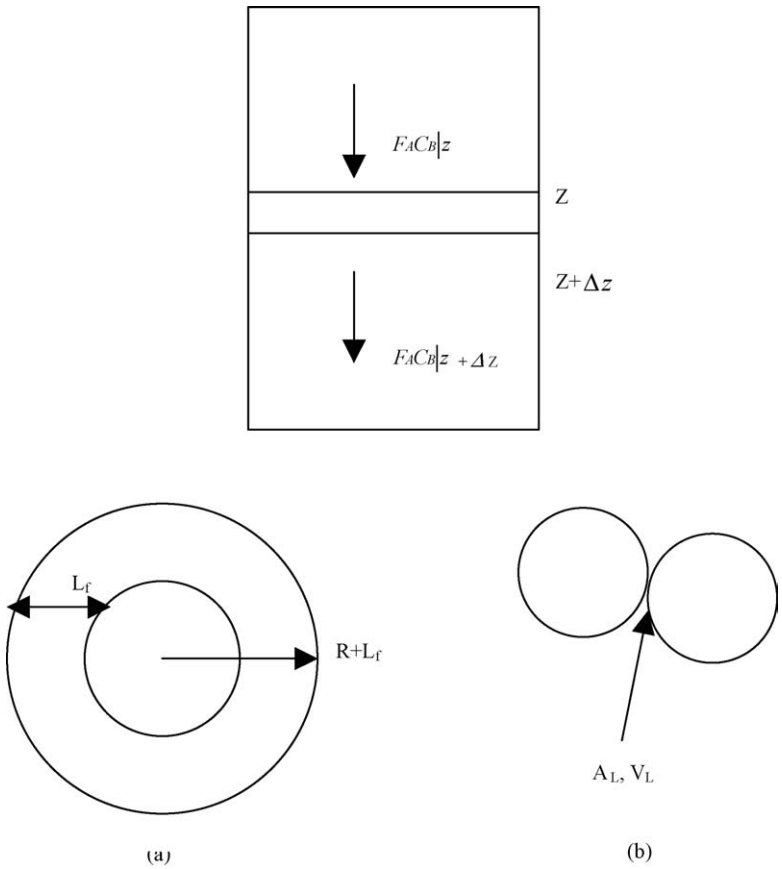

Fig. 1. Schematic representation of the trickle bed bio-reactor and the packing materials. F_A, volumetric flow rate of the liquid stream; C_B, substrate concentration; Z, axial position within the reactor. (a) Characteristic sphere. R, radius of each packing sphere; L_f, bio-film thickness over each packing material. (b) Contacting pattern of the spheres. A_L, bio-film area loss per unit packing sphere in contact; V_L, bio-film volume loss per unit packing sphere in contact.

The Eqs. (1)–(6) have been solved using fourth order Runge–Kutta technique with the aid of a suitable C-program. The growth kinetic parameters, maximum specific growth rate and saturation constant K_s, have been determined by non-linear analysis of the experimental data obtained from experiments conducted in batch mode.

6. Results and discussion

The growth kinetics of *Rhodococcus* sp. as determined from classical Monod model include the values of K_s and $Y_{X/S}$ and are reported in Table 2.

Fig. 2 represents the plot of simulated and experimental values of bio-film thickness over the packing material at maximum feed rate or 0.5 dm^3/h against time with initial sulfur concentration as a parameter. With due course of reaction time, the bio-film thickness was found to increase with the increase in the initial sulfur concentration. This is because substrate degradation increases with the formation of more and more microbial growth as the reaction time increases. Here, the agreement between simulated and experimental data is satisfactory. In Fig. 3, simulated values of bed porosity have been plotted against time again with initial substrate concentration as the parameter. The experimental data have been plotted on the same figure. The figure reveals that the bed porosity decreases with the increase in initial substrate concentration. This can be easily explained because higher the substrate concentration more is the biomass formation leading to the increase in bio-film

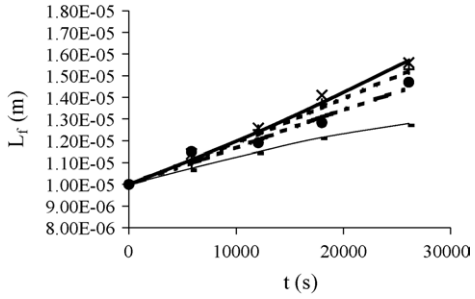

Fig. 2. Simulated (lines: (——) 540 ppm; (– · · –) 330 ppm; (· · ·) 430 ppm; (—) 200 ppm). Experimental (points: (×) 540 ppm; (●) 330 ppm; (+) 430 ppm; (–) 200 ppm). Simulated and experimental profiles of bio-film thickness against time with initial substrate concentration as parameter.

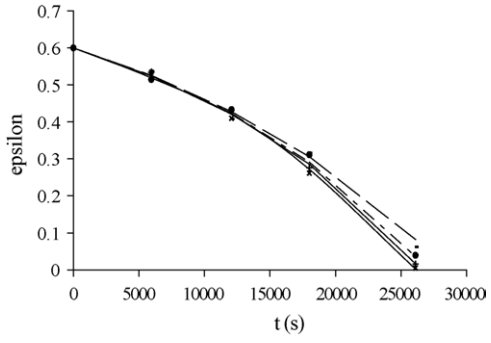

Fig. 3. Simulated (lines: (—) 540 ppm; (– - –) 330 ppm; (- - -) 430 ppm; (– – –) 200 ppm). Experimental (points: (×) 540 ppm; (●) 330 ppm; (+) 430 ppm; (–) 200 ppm). Simulated and experimental profiles of bed porosity against time with initial substrate concentration as a parameter.

density and hence decrease in bed porosity. From the close observation of the figure, it is evident that the experimental trend is well explained by the simulated results.

In Fig. 4, the simulated values of substrate concentration in the liquid phase at the minimum feed rate (0.25 dm^3/h) of diesel have been plotted against axial length of the reactor with initial sulfur concentration as a parameter. The experimental data have been superimposed on the same plot. As expected, the substrate concentration decreases with the axial length of the trickle bed reactor. The simulated data follow the same trend. Fig. 5 represents the simulated concentration profile of substrate against axial length of the reactor at different flow rates for initial sulfur concentration of 200 ppm. The flow rate of diesel was varied in the range of 0.25–0.5 dm^3/h. The corresponding experimental values have been plotted on the same figure. The simulated values are found to justify the experimental results. Close analysis of the figure reveals that the value of sulfur concentration in the reactor exit stream increases, i.e. the ultimate sulfur conversion decreases with the increase in the flow rate. At the lowest inlet diesel flow rate of 0.25 dm^3/h, the sulfur removal efficiency of 95.46% has been predicted by the mathematical model, whereas the corresponding experimental value is 95%. Similarly, the

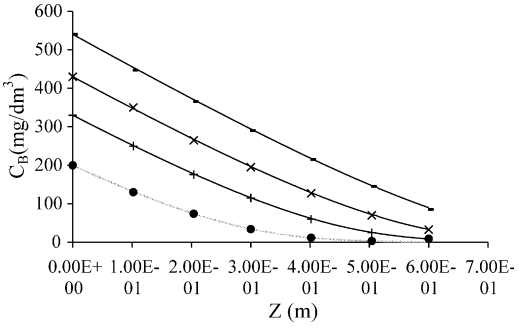

Fig. 4. Simulated (lines: (—) 540 ppm; (- - -) 330 ppm; (– – –) 430 ppm; (· · ·) 200 ppm). Experimental (points: (×) 430 ppm; (●) 200 ppm; (+) 330 ppm; (–) 540 ppm). Simulated and experimental profiles of substrate concentration against axial length of the reactor.

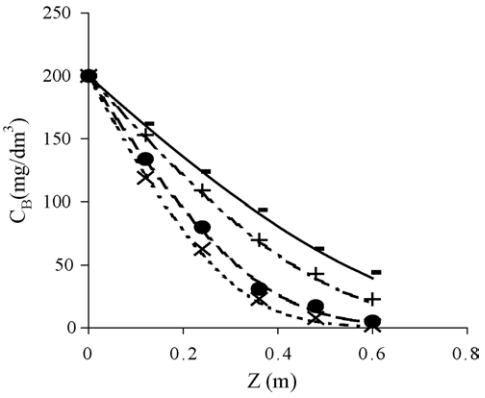

Fig. 5. Simulated (lines: (- - -) 540 ppm; (– · · –) 330 ppm; (—) 430 ppm; (· · ·) 200 ppm). Experimental (points: (×) 0.25LPH; (●) 0.3LPH; (+) 0.4LPHm; (–) 0.5LPH). Simulated and experimental profiles of substrate concentration against axial length with volumetric flow rate as a parameter with initial substrate concentration 200 ppm.

simulated and experimental values of sulfur removal efficiency corresponding to the feed rate of 0.5 dm^3/h are 80 and 77.8%, respectively. This is, however, expected as the increase in flow rate implies the decrease in reactor residence time causing drop in the ultimate conversion of the reactant. In this case also, the simulated trend can explain the experimental one. However, in all the figures at higher initial concentration of sulfur in diesel a little deviation of the simulated results from the experimental data has been noticed. This may be due to the idealistic assumptions like absence of mass transfer resistance etc. in the model.

7. Conclusions

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 concentration was varied in the range of 200–540 ppm. A trickle bed reactor was studied with the liquid flow rate and inlet sulfur concentration as parameters. A mathematical model capable of describing the bio-desulfurization of diesel in a trickle bed reactor has been proposed. 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: presence of external mass transfer resistance, etc. prevailing in the actual system.

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