Investigating the Kinetics of Biodesulfurization of Diesel

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Abstract

The technology of biodesulfurization requires that reactors, where the reaction can take place, must be designed. In order to do this, the kinetics of the process must be thoroughly understood. This work aims to investigate the kinetics of biodesulfurization of diesel. This was done by simulating the kinetics of the process alone and then with and without the effect of mass transfer. The kinetic parameters, maximum rate constant, v_{max}, and the Michaelis-Menton constant, $K_{M,}$ were estimated using the linear equations of Hanes, Lineweaver-Buck and Eadie-Hofstee. The values obtained for each of the parameters from the linear equations were close but are not the same. This necessitated the need to carry out a non-linear regression analysis on the substrate concentration-time data. The analysis was done using Marquardt's algorithm of non-linear regression analysis. The obtained results were then compared with experimental data, they both showed good correlation with the experimental data although the mass transfer influenced kinetics showed a better agreement with the experimental data. Based on the aforementioned findings, one may conclude that mass transfer played an important role in the kinetics of biodesulfurization of diesel.

Keywords: *Marquardt's algorithm, non-linear regression analysis, parameter estimation, biodesulfurization, mass transfer, diesel, kinetics and reactor.*

Introduction

Biodegradation kinetics is used to predict concentrations of chemical substances remaining at a given time during *ex-situ* and *in-situ* bioremediation processes. In most cases, the predicted information is based on loss of parent molecule targeted in the process (Segel and Slemrod 1989).

The key interest is frequently the decrease in toxicity concentration. Nevertheless, toxicity measurements require bioassays, which are always very difficult and tedious. Therefore, the efficacy of biodegradation is based on chemical measurements, e.g. disappearance of parent molecule, appearance of mineralization products or disappearance of other compounds used stoichiometrically during the biodegradation of a compound, for instance, electron acceptors (Nelson and Cox 2000). There are several scenarios by which a compound can be transformed biologically. This includes when the compounds serve as a source of carbon and energy, electron acceptor, and source of other cell components. Other scenarios are the transformation of a compound by non-growing cells (the compound does not support growth) and the transformation of a compound by co-metabolism, that is, transformation of a compound by cells growing on other substrate. The simplest case is where

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the compound serves as a source of carbon and energy for the growth of a single bacterial species. The compound is assumed to be water-soluble, non-toxic and other substrates or growth factors are not limiting (Stroppolo *et al*. 2001).

Biochemists and other interest groups usually analyze kinetics parameters within the Michaelis-Menton framework. In particular, the reversible reaction between enzyme E and substrate S, giving the enzyme-substrate complex ES, which irreversibly yields product P, has been extensively studied and resulted in the Michaelis-Menton equation (Michaelis and Menton 1913):

$$r = (v_{max} \cdot C)/(K_M + C), \quad (1)$$

where r is the rate of the substrate consumption, C is the substrate concentration, and K_M is the Michaelis-Menton constant.

A simple expression for an enzyme-catalyzed reaction can be illustrated as shown below

$$E + S \rightleftharpoons ES \rightarrow E + P. \quad (2)$$

The Michaelis-Menton equation allows one to estimate the reaction parameters, namely v_{max}, which is the maximum velocity of the reaction. The Michaelis-Menton equation assumes a single-enzyme single-substrate system. It does not consider the various steps involved in the transformation of the substrate to the product, assuming the substrate to be soluble and thus readily available to the organism (Grima and Schnell 2007).

Kinetic equations, which describe the activity of an enzyme or a microorganism on a particular substrate, are crucial in under-standing many phenomena in biotechnological processes. Quantitative experimental data is required for the design and optimization of biological transformation processes. A variety of mathematical models have been proposed to describe the dynamics of metabolism of compounds exposed to pure cultures of microorganisms or microbial populations of natural environment (Minton 2001). The characterization of the enzyme or microbe-substrate interactions involves the estimation of several parameters in the kinetic models from experimental data. In order to describe the true behaviour of the system, it is important to obtain accurate estimates of the kinetic parameters in these models (Olsen 2006).

Both derivative and integrated forms of equations derived for enzyme catalyzed reactions have been used to estimate kinetic parameters of microbiological processes. Estimates of kinetic parameters v_{max} and K_M have been calculated by fitting data to either integrated (Goudar and Devlin 2001) or derivative (Acuña-Argüelles *et al*. 2003) forms of the Michaelis-Menton and Monod equations (Monod 1949). Different approaches have been proposed for estimating the kinetic parameters, but progress curve analysis is the most popular because substrate depletion or product formation data from a single experiment are enough for parameter estimation (Duggleby and Wood 1989). In this approach, substrate depletion or product formation-time course is used in the integrated form of the kinetic model for parameter estimation. Some of these differential and integral equations can be found in the paper of Goudar and Devlin (2001).

It is important to note that most kinetic models and their integrated forms are nonlinear. This makes parameter estimation relatively difficult (Zhou *et al*. 2008). However, some of these models can be linearized. Various linearized forms of the integrated expressions have been used for parameter estimation. However, the use of a linearized expression is limited because it transforms the error associated with the dependent variable making it not to be normally distributed, resulting inaccurate parameter estimates (Olsen 2006). Therefore, nonlinear least-squares regression is often used to estimate kinetic parameters from nonlinear expressions. However, the application of nonlinear least-squares regression to the integrated forms of the kinetic expressions is complicated. This problem and its solutions were discussed by Goudar and Devlin (2001). The parameter estimates obtained from the linearized kinetic expressions can be used as initial estimates in the iterative nonlinear least-squares regression using the Levenberg-Marquardt method (Levenberg 1944; Marquardt 1963; Susu 1997).

The kinetics biodegradation rate of pharmaceutical and personal care products was

investigated by Gieratowska (2010) and it was found out that the kinetics followed a first-order rate. The half-lives of these products were also investigated. The kinetics of polyaromatic hydrocarbons, PAH by *Sphingomonas paucimobilis EPA 505* was modelled in engineered and natural systems based on probabilistic and statistical criteria, and Dimitriou-Christidis and Autenrieth (2007) inferred that the underlying interaction mechanism based on the model fits. The model was fully predictive and relied only on parameters determined in the sole PAH experiments. However, Knightes and Peters (2006) reported that the sole substrate model is inadequate to describe multi-substrate kinetics of a broad range of PAH mixtures. The potential of *Pseudomonas fluorescence* to degrade synthetic phenol in water was investigated by Agarry and Solomon (2008). It was observed that the culture followed substrate inhibition kinetics while the specific phenol consumption rates fitted the Haldane's model (Haldane 1930) based on which the bio-kinetic parameters were estimated. Orthogonal collocation and the Gear's method (Gear 1971) were used to model the kinetics of phenolic waste water biodegradation by Lin and Hsien (2009). Their simulated results agreed with the experimental ones. Moliterni *et al.* (2012) used simple Monod-type kinetic model to simulate the biodegradation of diesel fuel by some consortium of microorganisms. Their results revealed that the consortium of organisms function at high hydrocarbon concentrations. The biodegradation kinetics of benzene and toluene were modelled separately and as a mixture by Trigueros *et al*. (2007). Their work showed that a better description of pure substrate can be achieved by the Andrews' model (Andrews 1974) while mixtures could be best modelled with sum kinetics interaction parameters (SKIP) models.

Aribike *et al*. (2008) reported the ability of *Desulfobacterium indolicum* which was isolated from petroleum product contaminated soil in Lagos, Nigeria to selectively remove sulfur from kerosene. The kinetics of biodesulfurization of kerosene by *Desulfobacterium indolicum* was modelled by Kareem *et al*. (2013a). They found out the inadequacy of linearizing Michaelis-Menton equation to estimate bio-kinetic parameters of the process, they estimated the parameters by using the Marquardt's non-linear regression analysis. They found out that the kinetics was influenced by mass transferred. The broad substrate specificity of the microorganism for refined petroleum products was reported by Kareem *et al*. (2012) when they found out that it can also biodesulfurize diesel. The biodesulfurization of diesel by the microorganism was also modelled by Kareem *et al*. (2013b), this time around; the bio-kinetics parameters were estimated by direct integration of the Michaelis-Menton equation. The results gave good approximation of the concentration-time profile and the kinetics were also found to be mass transfer influenced.

In this study, the biodesulfurization kinetics was investigated, the parameters were estimated and then subjected to Marquardt iterative non-linear least-squares regression (Marquardt 1963). The obtained bio-kinetic parameters were used to model the biodesulfurization of diesel by *Desulfo-bacterium anilini*.

Materials and Methods

Marquardt's Algorithm

The iterative method for estimating the kinetic parameters v_{max} and K_M using the Marquardt's algorithm (Marquardt 1963) of non-linear regression analysis entails that the multi-response nature of the problem will be accounted for by the minimization of the sums of the squares of the residuals Φ on the molar quantities of the reaction (Chang *et al*. 2000).

The minimization of the sum of squares of the residuals can be represented by:

$$\Phi = \sum_i \sum_j (F_j^0 - F_j)_i^2 , \qquad (3)$$

where: i = 1,..., L (L = number of experiments), j = 1,..., N (N = number of components), F_j^0 = experimental molar quantity, and F_j = predicted molar quantity.

In this procedure, the parametric corrections δ were evaluated by solving the following set of equations:

$$(\mathbf{A}^T\mathbf{A} + \lambda\mathbf{I})\boldsymbol{\delta} = \mathbf{A}^T\mathbf{e}, \qquad (4)$$

where

$$\mathbf{A} = \begin{bmatrix} \frac{\partial F_1}{\partial k_1} & \frac{\partial F_1}{\partial k_2} & \frac{\partial F_1}{\partial k_3} \\ \frac{\partial F_2}{\partial k_1} & \frac{\partial F_2}{\partial k_2} & \frac{\partial F_2}{\partial k_3} \\ \frac{\partial F_3}{\partial k_1} & \frac{\partial F_3}{\partial k_2} & \frac{\partial F_3}{\partial k_3} \end{bmatrix}, \quad (5)$$

$\mathbf{A}^T$ is the transpose of matrix **A**, **e** = vector of differences between experimental and predicted molar quantities,

$$\mathbf{e} = \begin{bmatrix} \Delta k_1 \\ . \\ . \\ . \\ \Delta k_m \end{bmatrix}, \quad (6)$$

λ is an arbitrarily chosen scalar quantity, **I** is an identity matrix, and

$$\boldsymbol{\delta} = \begin{bmatrix} \Delta k_1 \\ \Delta k_2 \\ \Delta k_3 \end{bmatrix}. \quad (7)$$

The partial derivatives $\partial F_j/\partial k_m$ are evaluated using the following discrete approximation:

$$\frac{\partial F_1}{\partial k_1} = \frac{F(k_1,....,k_m) - F_1(k_1 + gk_1,....,k_m)}{gk_1}, \quad (8)$$

where g takes an arbitrary value suitable for the iterations.

For the algorithm:

- Some initial set of kinetic parameter values was assumed.
- The vector of residuals **e** was estimated using Eq. (6).
- The elements of matrix **A** were estimated using Eq. (5).
- Then $\mathbf{A}^T$ was estimated.
- Equation (4) was solved for **e** for the parametric correction vector, δ.
- Φ was estimated using Eq. (3).
- The kinetic parameters were upgraded according to Eq. (9) below:

  $k_m = k_m + \Delta k_m$. (9)
- The whole procedure was repeated until the termination condition was satisfied

The techniques resulted in good estimates of the rate constants.

Model Development

In the development of the kinetics of the sulfur-specific reductive pathway of biodesulfurization, the mechanism adopted is that in which dibenzothiophene (DBT) is used as the sole electron acceptor and sulfur is removed selectively (Kim *et al*. 1995). Biphenyl was found as the major reaction product. It is a single step reaction:

$$S \xrightarrow[E]{H} P, \quad (10)$$

where P is the biphenyl and H is the hydrogen.

Hence, the rate of DBT disappearance is given by:

$$r(C) = -\frac{dC}{dt} = \sum_i \frac{\nu_{\max,i} C_i}{K_{M,i} + C_i}. \quad (11)$$

Equation (11) represents the kinetics of the sulfur-specific reductive pathway of biodesulfurization since diesel is a multi-component feed for the microorganisms.

Mass Transfer

This is done by taking the mass balance of the substrates, the sulfur containing hydrocarbons in the fuel, and diesel, which is presented as follows. The material balance on the solute (substrates in diesel) over the time period from t to $t + \Delta t$ over the element of volume of a batch reactor from z to $z + \Delta z$ is thus obtained:

(Input at z) - (Output at $z + \Delta z$) - (Reaction due to biodesulfurization) - (Rate of transfer to the cell surface) = Accumulation over time period. (12)

In a batch reactor, there is no inflow or outflow of material, therefore:

(Accumulation over time period) = (Rate of transfer of the substrate to the cell surface) - (Reaction due to biodesulfurization). (13)

The mass transfer rate to the solid is:

$r_m = ak_L(C - C_S)A\Delta z$. (14)

The accumulation in the fluid phase is:

$r_{ac} = A\Delta z\ (dC/dt)$. (15)

There is no reaction in the fluid phase in the reactor since all the reactions take place on the cell surface, hence the reaction term is equal to zero.

Substituting Eqs. (14) and (15) into Eq. (12) gives:

$$k_L a(C - C_S)A\Delta z = A\Delta z\left(\frac{dC_i}{dt}\right), \qquad (16)$$

and dividing Eq. (16) by $A\Delta z$ results in

$$k_L a(C - C_S) = \frac{dC}{dt}, \qquad (17)$$

where C_S is the concentration of the substrate on the surface of the organism and is not easily measurable.

The solution to the problem can be obtained by applying the law of conservation of mass to the adsorbable solute contained in the fluid phase and the solid. It should be noted that the adsorption transfers material from the fluid phase and adds to the solid phase (the microorganism, *Desulfobacterium anilini*). The solid phase loses material by desulfurization and generates none.

Then the solid phase mass balance for the sulfur specific reductive pathway of biodesulfurization is:

$$A\Delta z\frac{dq}{dt} - A\Delta z r(c) = k_L a(C - C_S)A\Delta z\,. \qquad (18)$$

Dividing Eq. (18) through by the elementary volume, $A\Delta z$, yields Eq. (19):

$$\frac{dq}{dt} - r(C) = k_L a(C - C_S). \qquad (19)$$

Substituting Eq. (19) into Eq. (17) gives:

$$\frac{dq}{dt} - r(C) = \frac{dC}{dt}. \qquad (20)$$

The solutions to Eq. (20) are simple when q is a linear function of C, that is, the adsorption, is assumed to be linear. Then dq/dt can be replaced by $-K\,dC/dt$. Then:

$$\frac{dq}{dt} = K\frac{dC}{dt}, \qquad (21)$$

where K is a distribution coefficient.

Substituting $r(C)$ from Eq. (11) into Eq. (21) yields:

$$\frac{v_{\max}C}{K_M + C} = -(1+K)\frac{dC}{dt}. \qquad (22)$$

The distribution coefficient, K, was estimated using a model developed by Arey and Gschwend (2005) for sulfur-containing organic substances in the fuel phase. It is represented as:

$$\log K_{i,fw} = \log\left[\frac{RT}{V_f P_i^0}\right] - \left(C_{aw} + r_{aw}R_2 + S_{aw}\Pi_2^H + a_{aw}\alpha_2^H + b_{aw}\beta_2^H + V_{aw}V_x\right). \qquad (23)$$

The parameter R_2 describes the excess molar refraction of solute i, Π_2^H describes the polarity/polarizability of solute i, α_2^H describes the hydrogen-bonding acidity of solute i, β_2^H describes the hydrogen bonding basicity of solute i, and V_x describes the group-contributable molecular volume of solute i, while c, r, s, a, b, and v are adjustable coefficients specific to the two-phase system, in this case air and water. It is difficult to generate a substrate concentration-time data from Eqs. (11) and (22) because of their implicit nature. Such a profile can be obtained by using any numerical techniques. The Implicit Finite Difference Method was used to obtain a substrate concentration-time data from Eqs. (11) and (22) as a matter of convenience and because it is accurate, consistent and stable. Equations arising from an implicit method are difficult to solve, but their solution is not restricted by stability criteria. There is also no restriction on the size of the time step, Δt. The results were presented in terms of percentage biodesulfurization-time profile. The level of agreement between the simulated and experimental data was determined by the sum of variances between the sets of data. When this is done: the lower the sum, the better the agreement.

Results and Discussion

The kinetic parameters for the biodesulfurization of diesel by *Desulfobacterium anilini* were estimated by subjecting the experimental data to kinetic analysis. The experimental data were subjected to all the linear kinetic equations, namely, the Hanes (Hanes 1932), Lineweaver-Buck (Lineweaver and Buck 1934) and Eadie-Hofstee (Eadie 1942; Hofstee 1959) plots. The obtained values of v_{max} and K_M are shown in Table 1. These transformations are unsatisfactory as they can result in artificial weighting of the data leading to erroneous estimates of v_{max}

and K_M. In order to forestall this development, the experimental substrate concentration-time data was subjected to non-linear regression analysis.

It was observed that, at all instances, the parameters obtained from the linear equations are not the same for a particular set of data. It must be mentioned that the differences in the obtained values may seem insignificant. The curiosity, however, is borne out of some instances where the maximum rate constants, v_{max}, for biodesulfurization of dibenzothiophene (DBT) in diesel by *Desulfobacterium anilini* are not the same as obtained from the Hanes and Eadie-Hofstee equations (6.116 and 6.114 mg/L.hr) but the obtained Michaelis-Menton constants, K_M, are the same (182.1 mg/L). Instances where the maximum rate constants were found to be the same for varied Michaelis-Menton constants were also observed. The parameters estimated (Hanes and Eadie-Hofstee equations) with data obtained from benzothiophene (BT) biodesulfurization by *Desulfobacterium anilini* are a clear illustration of this phenomenon.

Table 1. Estimated kinetic parameters for the biodesulfurization of diesel.

	Hanes equation	Line-weaver-Burk equation	Eadie-Hofstee equation
Maximum rate constant, v_{BT}, mg/L.hr	0.554	0.547	0.554
Maximum rate constant, v_{DBT}, mg/L.hr	6.116	6.110	6.114
Michaelis-Menton constant, $K_{M,BT}$, mg/L	18.650	18.380	18.620
Michaelis-Menton constant, $K_{M,DBT}$, mg/L	182.1	181.9	182.1

The main challenge now is the choice of the correct linear models for parameter estimation, hence the need to seek a modification or an outright alternative of the parameter estimation since the Michaelis-Menton equation from which the linear equations were obtained is not a linear equation. In this work, a modification was done by carrying out a non-linear regression analysis on the obtained parameters from the linear plots using the Marquardt's algorithm.

The kinetic parameters from the Marquardt's algorithm are shown in Table 2 and are used in the simulation done in this work. The ones obtained from the linear plots were used as the initial guess (seeding). The solution of Eq. (23) gives rise to Table 3.

Table 2. Kinetic parameters obtained from the non-linear regression analysis using the Marquardt''s algorithm.

	v, mg/L.hr	K_M, mg/L
Benzothiophene	0.572	18.050
Dibenzothiophene	6.118	182.278

Table 3. The distribution coefficient of some sulfur-containing organic compounds in diesel.

	Distribution coefficient, K
Benzothiophene	2.312
Dibenzothiophene	2.038

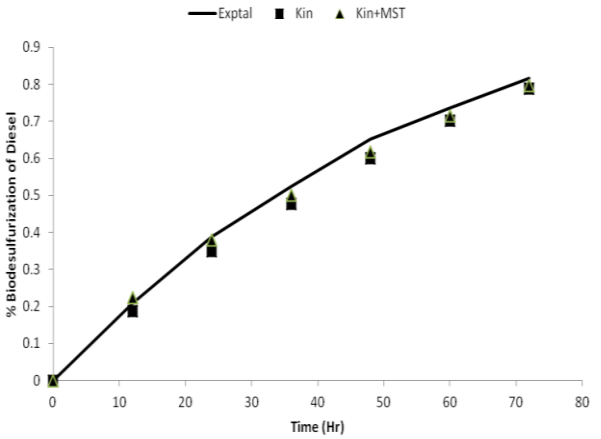

Fig. 1. The experimental and simulated percentages of diesel biodesulfurization-time profile by *Desulfobacterium anilini*.

Figure 1 shows the comparison of experimental and simulated percentage of biodesulfurization-time profiles based on kinetics with and without mass transfer models by *Desulfobacterium anilini*. It is important to mention that the growth kinetics of the organisms was neglected. This is because the

population densities of the organisms did not increase significantly during the biodesulfurization experiments as reflected by the optical density measurements (initial value, 0.930, and final value, 0.936, at a wavelength, λ, of 510 nm) and by standard plate counts (initial value, 6.40×10^6, and final value, 6.44×10^6 cfu/ml) (Kareem 2010). It is plausible to say that the sulfur compounds were probably utilized by the organisms to synthesize some amino acids such as methionine and cysteine required for sustenance and not necessarily for procreation.

The sums of variances between the experimental and simulated data of kinetics without mass transfer and that with mass transfer are 8.898×10^{-3} and 2.77×10^{-3}, respectively. This is clearly shown in Table 4. Figure 1 shows the graphical comparison. It can be seen that there is a good agreement among them. However, there is a better agreement between the mass transfer influenced kinetics than that which is plain kinetics. The kinetics of chemical analyses of catalytic reactions without the incursion of transport processes is a normal practice for two main reasons.

Table 4. Sums of variances between the simulated and experimental percentages of diesel biodesulfurization.

Time (hours)	Kinetics	Kinetics + Mass Transfer
0	0	0
12	4.41×10^{-4}	2.89×10^{-4}
24	1.521×10^{-3}	7.23×10^{-5}
36	2.304×10^{-3}	5.52×10^{-4}
48	2.601×10^{-3}	1.056×10^{-3}
60	1.19×10^{-3}	4.2×10^{-4}
72	8.41×10^{-4}	3.8×10^{-4}
Sum	8.898×10^{-3}	2.77×10^{-3}

In the first place, if fundamental knowledge of a reaction is available through the mechanism of the reaction, it will enhance the chances of catalyst design that will take advantage of the optimal reaction pathways to the desired products.

Secondly, the usual procedure for reactor design of an industrial process involves the coupling of the intrinsic rate kinetics of the reaction with the transport relationships. These relationships are important for industrial processes since any of the various diffusion processes may be the limiting factor(s).

Conclusion

The good agreement between simulated and experimental data goes to show that the assumptions made in developing the models are correct. The implication is that the estimated and measured kinetic parameters used in developing the models are acceptable and can be used in reactor design for biodesulfurization. The kinetics of biodesulfurization of diesel by *Desulfobacterium anilini* has been found to be mass transfer driven. Thus the technology is getting closer to the marketplace.

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