

## **Anaerobic Biodesulfurization of Kerosene Part II: Investigating Its Kinetics**

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**Abstract:** Extensive research works have been carried out on biodesulfurization, especially which of dibenzothiophene as a model sulfur compound in petroleum. Recently, biodesulfurization of real petroleum feed, mostly diesel have been reported. The biodesulfurization of kerosene is hardly reported because it is mostly combusted domestically especially in sub-sahara Africa including Nigeria. The capability of *Desulfatiglans anilini comb. nov.* to desulfurize kerosene has been reported by authors elsewhere. This work examines the kinetics of kerosene biodesulfurization with and without the influence of mass transfer. The bio-kinetic parameters were estimated using the various methods of Hanes, Lineweaver-Buck and Eadie-Hofstee, all from the linear transformation of Michaelis-Menten equation. The obtained results when compared caused confusion, thus, the Michaelis-Menten equation was integrated and the bio-kinetic Parameters were estimated thereof. The partition coefficients of sulfur containing hydrocarbons in kerosene and in water was used instead of mass transfer coefficient, this was done using the Arey and Gschwend model. The developed model equations were solved numerically using the Finite Difference Method. The simulated results were compared with available experimental data, a good agreement was observed. The result showed that mass transfer played a significant role on the kinetics of the process.

**Keywords:** Bio-kinetic Parameters, Finite Difference Method, Linear Solvation Energy Relationships (LSERs), Log Mean Concentration Difference (LMCD) and Mass Transfer.

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### **I. Introduction**

Every day, about 80 million barrels of crude oil are mined from the Earth. There is no indication that this rate will be reduced any time in the nearest future, recent estimates of the worldwide reserves of fossil fuels [1] indicated that the proven reserves of natural gas, crude oil, bitumen and coal are sufficient to continue at this rate for at least the next 70 years. About 90% of the hydrocarbons mined from the earth are burnt for energy. Since most liquid and solid (i.e. oil and coal) reserves are contaminated with sulfur, direct combustion of this fuel would lead to the release of vast amounts of sulfur oxides into the atmosphere. These oxides are the principal source of acid rain and most countries have imposed regulations to control their release [2]. These regulations come in the form of limiting sulfur emissions from power plants attainable by using low sulfur fuels and the imposition of increasingly stringent restrictions on the levels of sulfur allowed in transportation fuels (such as jet fuel and diesel) and home heating oil. More recently, sulfur in gasoline has also been targeted, since the sulfur oxides produced from the combustion of gasoline poison the catalytic converters on automobile exhaust systems. These converters are used to combust un-burnt hydrocarbons in the engine exhaust, which contribute significantly to urban pollution. As a result, the United States Environmental Protection Agency and other regulatory agencies have moved to eliminate sulfur completely from gasoline in order to stop the poisoning of these inorganic catalysts [2].

Extensive researches on sulfur selective pathways have focused on model compounds most especially DBT. Scanty work has been reported on the biodesulfurization of real refinery feeds and some petroleum products limiting the ability to assess the commercial potential of biodesulfurization. The few real refinery feeds researches have focused on diesel due to its prominent role in transportation and industries [3]. The kinetic analysis of biodesulfurization of model oil containing multiple alkyl dibenzothiophenes was investigated by [4], their result showed that substrates inhibit desulfurization and its kinetic was well predicted by a Michaelis-Menten competitive inhibition model, furthermore, their result showed that the desulfurization rate decreased in the multiple alkyl dibenzothiophenes system compared to a single alkyl dibenzothiophene system. The study of pore structure characteristics of high sulfur coal by nitrogen method was investigated by [5], they used the fractal geometric theory and found out that specific surface area as well as the pore volume increase with decreased particle diameter, also sulfur content of the coal decrease with decreased particle diameter. [6] investigated the kinetics of oxidative desulfurization of sulfur compounds in diesel; synthesized polyoxometalates were used as catalysts in the presence of  $H_2O_2$  to oxidize derivatives of benzothiophene in model gas oil. The process was combined with solvent extraction. They were able to remove 98% of sulfur and recover about 90% of the oil.

Kerosene is a thin, clear, liquid hydrocarbon fuel distilled from petroleum, it is also known as Paraffin or Paraffin oil in countries such as United Kingdom, Ireland, Hong Kong and South Africa. It finds uses in heating and lighting, cooking, transportation and entertainment. It has also been found to be a good pesticide, industrial solvent and can be used medically to store crystals [7].

Kinetic equations, which describe the activity of an enzyme or a microorganism on a particular substrate, are crucial in understanding 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 [8]. Characterization of the enzyme or microbe-substrate interactions involves 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 [9].

The derivative and integrated forms of equations derived for enzyme catalyzed reactions have been used to estimate kinetic parameters of microbiological processes. Kinetics parameters of enzyme catalyzed reactions are estimated within the Michaelis-Menten framework. The Michaelis-Menten equation allows one to estimate the reaction parameters namely  $V_{max}$  which is the maximum velocity of the reaction,  $K_M$  the Michaelis-Menten constant. It assumes a single-enzyme single-substrate system; it does not consider the various steps involved in the transformation of the substrate to the product and finally assumed the substrate to be soluble and thus readily available to the organism [10].

It is important to note that most kinetic models and their integrated forms are nonlinear. This makes parameter estimation relatively difficult [11]. 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 linearized expression is limited because it transforms the error associated with the dependent variable making it not to be normally distributed, thus inaccurate parameter estimates [9]. 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 solutions were discussed by [12]. 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 [13].

The objectives of this paper is to investigate the kinetics of biodesulfurization of kerosene by *Desulfatiglans anilini* comb. nov. considering whether mass transfer influences it or not. For this purpose, the following activities were performed: Michaelis-Menten equation was integrated, possible locations where mass transfer resistance was situated was sought, the mass transfer was coupled with Michaelis-Menten equation and the resulting equation solved numerically, bio-kinetic parameters were estimated using all the linearly transformed Michaelis-Menten equation and the simulated values from all the transformations were compared to known experimental values of kerosene biodesulfurization.

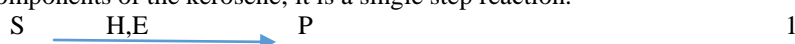
## II. Materials and Methods

### Kinetic Model Development

To develop the kinetic model, the anaerobic pathway of biodesulfurization of kerosene was chosen bearing in mind the multicomponent nature of its sulfur content. The Michaelis-Menten equation was integrated directly and kinetic parameters estimated. The possible location to mass transfer resistance was also sought and finally model equations were developed, the accuracy of the models were tested by comparing simulated values from them with known experimental values.

### Kinetics of Biodesulfurization

In the development of kinetic model of the biodesulfurization of kerosene, the sulfur specific reductive pathway of biodesulfurization was adapted. In the mechanism adopted, the sulfur-containing organic compound component of the kerosene is used as the sole electron acceptor and sulfur is removed selectively [14]. Biphenyl equivalent of the sulfur-containing organic compound was found as the major reaction product for each of the sulfur components of the kerosene; it is a single step reaction.



Where P is the biphenyl, S the substrate, E the enzyme acting on substrate and H is hydrogen. Hence, the rate of biodesulfurization is given below,

$$r(C) = -\frac{dC_i}{dt} = \sum_1^i \frac{v_{max,i} C_i}{K_{Mi} + C_i} \quad 2$$

$r(C)$  is the rate of substrate consumption,  $C$  is substrate concentration,  $V_{max}$  is the maximum rate constant of the reaction and  $K_M$  is the MichaelisMenten constant.

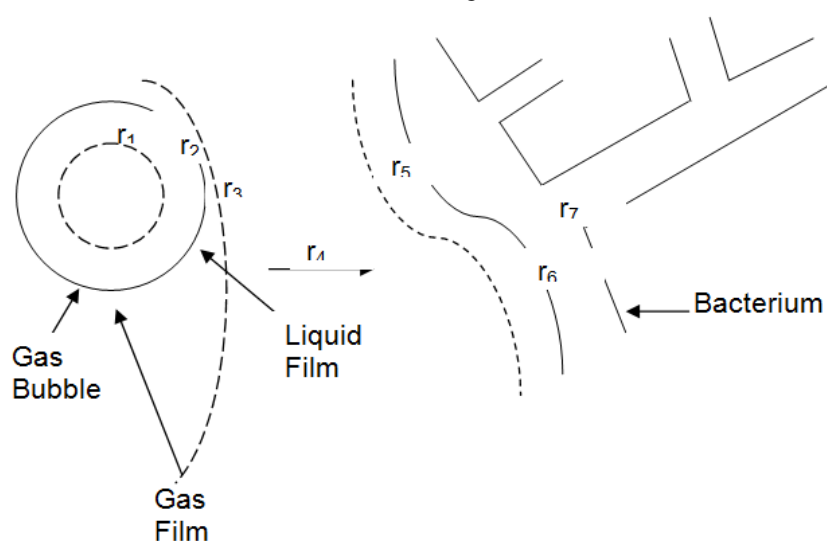
The various sulfur components in the kerosene were taken care of in the expression.

### Location of Mass Transfer Resistance

Resistances to mass transfer can be encountered at eight possible locations in a reactor, namely;

- (1) In the gas film;
- (2) At the gas/liquid interface;
- (3) In the liquid film surrounding the gas interface;
- (4) In the liquid phase containing the substrate;
- (5) In the liquid film surrounding the solid (microorganism);
- (6) At the liquid/solid interface;
- (7) The site of reaction;
- (8) In the solid phase.

A scheme of the reactor in which the model is based is shown in Figure 1



**Figure 1:** The Pathways of Hydrogen (The Gas Phase) and Substrate Transfer to a Microorganism in a Bioreactor

These resistances occur in series and the largest of them is the most significant and will be the rate-controlling. Thus, the entire mass transfer pathway can be modelled using a mass transfer correlation. Some of these resistances may not be rate-controlling because of the reasons advanced below. The developed model is based on the following assumptions:

1. Since gas-phase mass diffusivities are typically much higher than liquid phase diffusivities, the resistance of the gas film in the gas phase can be neglected relative to the liquid film surrounding the bubble.
2. The interfacial resistance to transport at the gas/liquid interface is negligible.
3. The resistance at the liquid/solid interface can thus be neglected as well.
4. Provided the liquid is well-mixed, transport through the liquid phase is generally rapid and bulk fluid resistance is neglected.
5. The resistance in the solid phase (microorganism) may also be neglected because the size of the substrate (the molecules of DBT and its derivative) is too large for permeability into the cytoplasm. Hence the enzymes are described as being extracellular.

Two mass transfer resistances and the reaction rate remain to be considered and these are the two liquid film resistances. Depending on the size of microbial particle, any one of these resistances may be controlling.

1. In the case of small microbial pellets, their very small size and hence large interfacial area relative to that of gas bubble will result in the liquid film surrounding the gas bubble being the rate determining step in transport.
2. On the other hand, large microbial pellets may be of a size comparable to that of a gas bubble and resistance in the liquid film surrounding the solid (microorganism) may dominate.

The resistance on the surface of the microorganism results from diffusion and reaction of hydrogen and the substrate. The overall rate of substrate conversion is governed solely by the kinetics of the reaction. However, if mass transfer is slow relative to reaction, transport may influence the observed kinetic rates. The role of the hydrogen in the reductive process is that of electron donor to the substrates. This implies that the substrate in the bulk liquid will diffuse to the surface of the cell where it is adsorbed and undergoes biodesulfurization. Equation 2 represents the kinetics of the sulfur specific reductive pathway of biodesulfurization since kerosene is a multi-component feed for the microorganisms.

### Parameter Estimation

A simple expression which accounts for enzyme-catalyzed reaction is

$$-r_A = r_R = -\frac{dC_A}{dt} = \frac{v_{\max} \cdot C_A}{K_M + C_A} \quad 3$$

Equation 3 can be rearranged and solve by homogeneous method

$$-\left(\frac{K_M + C_A}{C_A}\right) dC_A = v_{\max} dt \quad 4$$

$$-\int_{C_{A0}}^{C_A} \left(\frac{K_M + C_A}{C_A}\right) dC_A = v_{\max} \int_0^t dt \quad 5$$

The result of Equation 5 is

$$-\left[K_M \text{Log} C_A + C_A\right]_{C_{A0}}^{C_A} = v_{\max} t \quad 6$$

$$K_M \text{Log} \left(\frac{C_{A0}}{C_A}\right) + (C_{A0} - C_A) = v_{\max} t \quad 7$$

On rearranging Equation 7,

$$\frac{C_{A0} - C_A}{\text{Log} \left(\frac{C_{A0}}{C_A}\right)} = -K_M + \frac{v_{\max} t}{\text{Log} \left(\frac{C_{A0}}{C_A}\right)} \quad 8$$

The left hand side of Equation 8 may be called the Log Mean Concentration at any instant. The parameters for the sulfur-containing organic compound component of the kerosene were estimated using equation 8. The parameters were also estimated using the linear plots of Hanes, Lineweaver-Buck and Eadie-Hofstee and compared with those obtained from Equation 8.

Mass balance of the substrate in the liquid phase (kerosene) is done as previously described by [3] and the resulting equation is:

$$\text{where } \frac{v_{\max} C_i}{K_{Mi} + C_i} = -(1 + K_{Di, fw}) \frac{dC_i}{dt} \quad 9$$

$$\log K_{Di, fw} = \log \left[ \frac{RT}{V_f P_i^0} \right] - (C_{aw} + r_{aw} R_2 + S_{aw} \Pi_2^H + a_{aw} \alpha_2^H + b_{aw} \beta_2^H + V_{aw} V_x) \quad 10$$

The parameters  $R_2$  describes the excess molar refraction of solute i [15],  $\Pi_2^H$  describes the polarity/polarizability of solute i [16],  $\alpha_2^H$  describes the hydrogen-bonding acidity of solute i [17],  $\beta_2^H$  describes the hydrogen bonding basicity of solute i ([18] and [19]) and  $V_x$ , describes the group-contributable molecular volume of solute i [20] while  $c$ ,  $r$ ,  $s$ ,  $a$ ,  $b$ , and  $v$  are adjusted coefficients specific to the two-phase system, in this case air and water. Equation 10 is the Arey and Gschwend equation [21] and it accurately predicted fuel-water distribution coefficients of a wide range of non-polar hydrocarbon and thiophene compounds in agreement with previous findings [22]. However, predictions were highly unreliable for polar solutes. The Distribution coefficients obtained from the Arey and Gschwend equation for Thiophene and 2, 5- Dimethylthiophene are 1.281 and 1.054 respectively

The resulting differential equations, that is, equations 2 and 9 were solved numerically using the Implicit Finite Difference Method. The choice was guided most importantly by convenience. Furthermore, it is

accurate, consistent and stable. Equations arising from implicit method may be difficult to solve, but their solution using the Finite Difference Method is not restricted by stability criteria. There is also no restriction on the size of the time step. The simulated data were compared to the experimental data of the biodesulfurization of kerosene by *Desulfatiglans anilini* comb. nov.[3].

### III. Results and Discussions

The anaerobic route is a potentially attractive biodesulfurization route to apply, because of its sulfur specificity. Furthermore, the reaction pattern is similar to HDS. However, growth under anaerobic conditions proceeds slowly, the quality of its output outweighs its rate consideration. The sulfur components available for analysis in the kerosene were benzothiophene, dibenzothiophene, thiophene and 2, 5 - dimethylthiophene, however, only thiophene and 2, 5-dimethylthiophene were found to be present [3].

#### Estimated Parameters

The estimated parameters from the linear plots of Hanes, Lineweaver-Burk, Eadie-Hofstee and the direct integration of Michaelis-Menten are shown in Table 1. The data were obtained from experimental results of biosulfurization of kerosene by *Desulfatiglans anilini* comb. nov. [3].

The parameters obtained for the same data are not the same even though the difference is not much. For instance, the maximum rate constant is the same with all the methods but the Michaelis-Menten constants,  $K_M$  are not the same. The bone of contention is which of the methods arising from the linear transformation of the Michaelis-Menten equation can be chosen for reactor design or other purposes. The parameters obtained from the integration of the Michaelis-Menten equation were however used for the simulation of the biodesulfurization of kerosene by *Desulfatiglans anilini* comb. nov..

**Table 1.** The Estimated Kinetics Parameters from the Transformation of Michaelis-Menten Equation

Linear Transformations	Parameters	Thiophene	2, 5 – Dimethyl thiophene
	$V_{max}$ (mg/L.hr)	0.104	1.426
<b>Hanes-Woolf</b>	$K_M$ (mg/L)	0.556	6.760
<b>Lineweaver-Burk</b>	$V_{max}$ (mg/L.hr)	0.104	1.426
	$K_M$ (mg/L)	0.533	6.780
<b>Eadie-Hofstee</b>	$V_{max}$ (mg/L.hr)	0.104	1.426
	$K_M$ (mg/L)	0.554	6.780
<b>Integrated MichaelisMenten Equation</b>	$V_{max}$ (mg/L.hr)	0.104	1.426
	$K_M$ (mg/L)	0.548	6.700

The Hanes-Woolf plot known as Hanes plot for short is obtained by rearranging the Michaelis-Menten equation such that:

$$\frac{C}{v} = \frac{C}{v_{max}} + \frac{K_M}{v_{max}} \tag{11}$$

The transformation gives the best  $\frac{1}{v_{max}}$  instead of  $V_{max}$ , the main drawback of this transformation is the dependent of both abscissa and ordinate on the substrate concentration.

The Lineweaver-Burk plot is obtained by linearly transforming Michaelis-Menten equation to

$$\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{C} + \frac{1}{v_{max}} \tag{12}$$

The double reciprocal plot is prone to error because it distorts the error structure of the data.

In the Eadie-Hofstee plot, the Michaelis-Menten equation was linearly transformed such that the reaction rate is plotted as a function of the ratio between rate of reaction and substrate concentration:

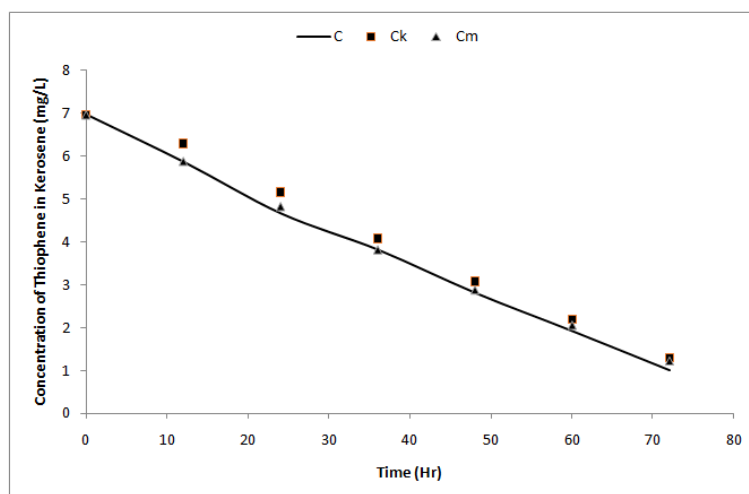
$$v = -K_M \frac{v}{C} + v_{max} \tag{13}$$

The abscissa and ordinates are independent variables, both dependent on reaction rate, so like the Hanes-Woolf plot, any experimental error will be present in both axes. Parameters estimated from this plot is more reliable than those of Eadie-Hofstee and Lineweaver-Burk because it gives equal weight to data points in any given range of substrate concentration or reaction rate. All these shortcomings may be attributed to the non-linearity of the Michaelis-Menten equation itself thus a non-linear regression method will give a better estimates of the kinetic parameters.

### Simulated Results

The simulated results were obtained by solving equation 8 for the solely kinetic modelling using the direct integration of the Michaelis-Menten equation. For the simulation of the incursion of mass transfer into kinetics, equation 9 was solved numerically using the Implicit Finite Difference Method. The results are shown in Figures 2, 3 and 4 for thiophene, 2, 5 – Dimethylthiophene and kerosene respectively. The level of agreement between the simulated and experimental data was determined by the sum of variances between the sets of data. The sum that is lower between two sets of data has a better agreement. It is important to mention that the growth kinetics of the organisms was neglected. This is because the population density of the organism did not increase significantly during the biodesulfurization experiments as reflected by the optical density measurements (Initial value, 0.930 and final value, 0.934 at a wavelength,  $\lambda$ , 510 nm and by standard plate counts (Initial value,  $6.40 \times 10^6$  and final value,  $6.43 \times 10^6$  cfu/ml). it is plausible to say that the sulfur compounds were probably utilized by the organisms to synthesise some amino acids such as methionine and cysteine required for sustenance and not necessarily for procreation.

Figure 2 shows the comparison of the simulated data with the experimental data of thiophene biodesulfurization. The simulated data consist of the simulated kinetic data alone and the ones simulated with mass transfer and kinetic. The variances were measured at time of 0, 12, 24, 36, 48, 60 and 72 hours and the sum of these variances was used to determine the level of agreement of the data.

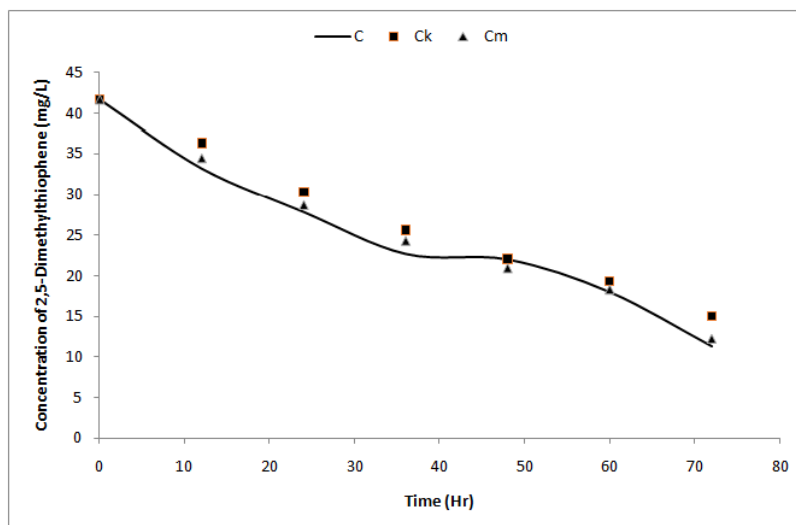


**Figure 2:** The Concentration – Time Profiles for Experimental and Simulated Thiophene Biodesulfurization in Kerosene

For thiophene, its concentration in the kerosene ranged between 1 to 6.955 mg/L and the variances at 12, 36 and 48 hours are almost zero for the data of simulated mass transfer influenced kinetics which is a very good agreement with the experimental value. The overall sum of variance was 0.107, the lowest being  $6.87 \times 10^{-5}$  at 36 hour and the highest was 0.051 at the 72<sup>nd</sup> hour. For the kinetics without mass transfer effect, the lowest variance was 0.076 at 48 hour while the highest was 0.188 at the 12<sup>th</sup> hour and the overall sum was 0.779. It was generally observed that the data of the mass transfer influenced kinetics has a better agreement than those without the effect of mass transfer. Based on the aforementioned, it may be inferred that the kinetics of thiophene biodesulfurization in kerosene by *Desulfatiglans anilini* comb. nov. is influenced by mass transfer.

It is worthy of note as to the need on why investigate kinetics with or without the incursion of mass transfer be studied separately, this is because kinetics of chemical analyses of catalytic reactions without the incursion of mass transfer is a normal practice to enable us know the mechanism of the reaction, this would enable catalyst design that will take advantage of optimal reaction pathways to the desired products. Furthermore, the coupling of intrinsic rate kinetics with transport relationships are important for industrial processes since any of them may be the rate limiting factor.

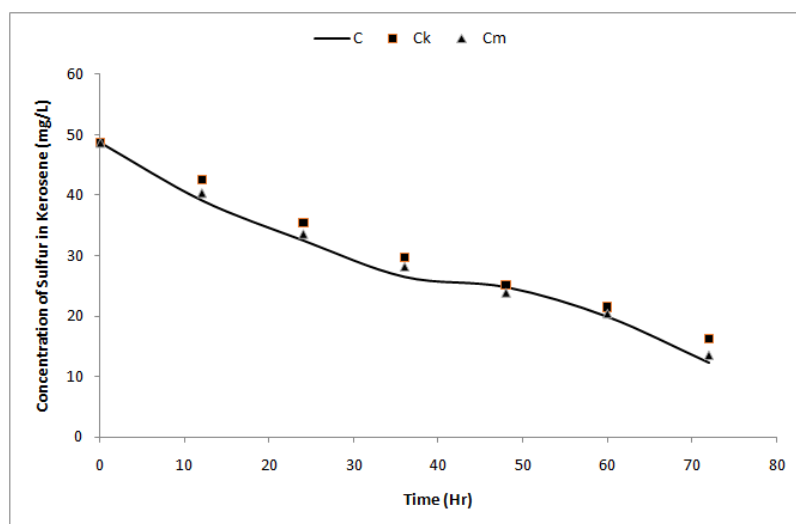
The simulated and experimental data for 2, 5 – Dimethylthiophenebiodesulfurization is shown in Figure 3. The variance for the kinetics data ranged between 0.002 at the 48<sup>th</sup> hour and 8.482 at the 36<sup>th</sup> hour.



**Figure 3:** The Concentration – Time Profiles for Experimental and Simulated 2, 5 – DimethylthiopheneBiodesulfurization in Kerosene

The sum of the variance from the experimental data is 38.249 on the other hand the variance of the simulated mass transfer influenced kinetics ranged between 0.099 at the 60<sup>th</sup> hour and 2.636 at the 36<sup>th</sup> hour, the sum here is 6.817, like for thiophene the kinetics is mass transfer driven. It is worthy of note that the concentration range in this process is between 11.323 mg/L and 41.724 mg/L. The mass transfer driven simulation data have a better agreement with the experimental data than the kinetics alone at all points considered except at the 48<sup>th</sup> hour where the simulated data of kinetics without mass transfer had a better agreement. It would be observed that the simulated kinetic data of thiophenebiodesulfurization than those of 2, 5 – Dimethylthiophene relative to the experimental data, this can be attributed to the fact that steric hindrances caused by presence of the two methyl groups that would play significant role in the biodesulfurization of 2, 5 – Dimethylthiophene was not considered in the development of the kinetic models.

The simulation of the kinetics of biodesulfurization of the sulfur content in kerosene by *Desulfatiglans anilini* comb. nov. is a case of single organism multiple substrate unlike that of thiophene and 2, 5 – Dimethylthiophenebiodesulfurization where is the case of the usual single microbe single substrate scenario. The result of the simulation is presented in Figure 4, it is assumed that only two types of sulfur, thiophene and 2, 5 – Dimethylthiophene are available to the organism, *Desulfatiglans anilini* comb. nov.. The sulfur content in kerosene ranged from



**Figure 4:** The Concentration – Time Profiles for Experimental and Simulated sulfur content in Kerosene

12.3025 mg/L to 48.679 mg/L, the variance of the simulated data of the kinetics without mass transfer incursion from the experimental data ranged from 1.243 at the 60<sup>th</sup> hour to 8.063 at the 72<sup>nd</sup> hour, the sum of the variance is 13.865. On the other hand, the variance of the simulated data of mass transfer influenced kinetics ranged from 0.212 at 60<sup>th</sup> hour to 2,662 at the 36<sup>th</sup> hour.

Its sum of variance was 6.343, it was observed that at all times, the simulated mass transfer influenced kinetic data had a better agreement with the experimental value that the data of the kinetics without the incursion of mass, transfer, consequently, one may conclude that the kinetics of kerosene biodesulfurization by *Desulfatiglans anilini* comb. nov. is influenced by mass transfer, the implication of this is that the substrate must be available to the microorganism for biodesulfurization to take place.

The concentration – time profile of thiophene is linear, this indicates a zero order kinetics. This means that the thiophene was biodesulfurized at a constant rate and the microorganism has a high affinity for the substrate, this has been demonstrated by the low Michaelis-Menten constant. The concentration – time profiles of 2, 5 - Dimethylthiophene and sulfur in kerosene are almost linear but for between the 36<sup>th</sup> and 48<sup>th</sup> hour. This may be attributed to the steric hindrances caused by the methyl groups at positions 2 and 5.

#### IV. Conclusion

It has been found that linear transformations of the Michaelis-Menten equation as provided by any of the plots of Hanes, Lineweaver-Burk and Eadie-Hofstee for the purpose of parameter estimation may not be adequate for reactor design as their comparison in this study showed that they do not give the same answer, the direct integration of Michaelis-Menten equation would provide a better kinetic parameters of bio reactions than those from plots Hanes, Lineweaver-Burk and Eadie-Hofstee. Furthermore, the simulated concentration – time profile of the mass transfer plus kinetics has a better agreement with the known experimental values that those with kinetics alone. The good agreement of simulated data and the experimental ones shows that the assumptions made in developing the models are valid. The kinetics of the biodesulfurization by *Desulfatiglans anilini* comb. nov. is influenced by mass transfer,

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