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Modelling Performance Evaluation of Microbial Desulphurization of Waterberg Steam Coal in CSTR

Seshibe Stanford Makgato*, Evans Martin Chirwa - Nkhalambayausi

Water Utilisation and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa
Makgato2001@yahoo.com

The first part of this study used microbial desulphurization process as a pre-combustion technique for sulphur content reduction in Waterberg steam coal. This is simulated at the laboratory scale where Continuously Stirred Tank Reactor (CSTR) acts as a biological reaction chamber. Experimental tests were performed by varying coal particle size distribution of -0.85 mm, +1.00 mm, +2.30 mm and 4.60 mm in order to determine the influence and optimum condition for desulphurization process. The second part of this study deals with developing a model based on reaction kinetics, simulate microbial desulphurization process in CSTR system and validate the model under various experimental conditions. Kinetics study and parameter estimations were evaluated and optimized using the Simulation Programme for Aquatic Systems (AQUASIM) 2.0 Software. The average kinetic parameters in the bioreactor were determined for both without inhibition: k_d = 1.65 x 10^{-3} (h^{-1}), K_s = 1.23 x 10^{-4} mgL^{-1}, X_0 = 523 mgL^{-1} and χ^2 = 0.524 and with inhibition, K_I = 371 mgL^{-1} for finer coal particle size. Equally important, these kinetic parameters were determined by means of optimization. Consideration should be given that the developed model may be applied to only wider range of sulphur content range studied.

1. Introduction

The supply of energy in South Africa continues to depend heavily on coal at the present time and will continue to do so the near future. Further deployment of renewable energy technologies in the region is hindered by concerns over high cost and unreliable electricity generation capacity. In South Africa, coal still stands as the most reliable, cheap and abundantly available energy source. Almost 95% of electricity generation in the country is from coal-fired power plants. However, the use of coal in electricity generation has attracted attention due to its sulphur content. Upon combustion, sulphur in the coal leads to sulphur dioxide (SO2) which have serious negative effects on plant and animal health, metallurgical and environment which may give rise to global warming (Mketo et al., 2016), acid rain (Hu et al. 2018) and water pollution. Additional issues including human health such as chronic respiratory illnesses (Mketo et al., 2016), sulphate aerosols from S(0)/S(-2) oxidation causing corrosion (Zhao et al., 2008), abrasion, fouling and slagging of metal bodies (Mketo et al., 2016) which result in boiler tubes leaks. Therefore, the removal of all sulphur forms in coal is essential to protect the environment and community properties. Several pre-combustion processes (viz. biological treatment, chemical and physical processes) and post-combustion desulphurization technologies have been reported in the literature.

Among variety of pre-combustion processes mentioned, biodesulphurization arises as a clean, efficient and environmental friendly technique which is having low capital and operating costs as well as being less energy intensive. It is therefore noticeable that certain bacteria exist with demonstrated strong abilities to oxidation and metabolism of sulphur in the coal and to utilize the energy released to support their growth. Many workers reported on the best performing pure culture which comprised of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. Knowledge of biokinetics is essential for microbial desulphurization system design and optimization of operational conditions. Therefore, in order to select and optimize the appropriate biodesulphurization treatment technology, it is important to have the knowledge of the kinetic parameters of the biological reactions concerned. In this study, a model was developed on a simulated medium sulphur type steam coal biodesulphurization in a CSTR system.

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2. Materials and methods

2.1 Coal samples and analysis

Coal samples were screened to – 0.85 mm, +1.00 mm, +2.30 mm and +4.60 mm particle sizes and sterilized prior to biodesulphurization treatment. Total sulphur content in coal samples of – 0.85 mm, +1.00 mm, +2.30 mm and +4.60 mm particle sizes were found to be 1.45 wt.%, 1.41 wt.%, 1.44 wt.% and 1.43 wt.% respectively. Finer coal particles below – 0.85 mm was not considered as fine coal particles are difficult to settle. On the other hand, good mixing environment is required for creating sufficient contact of coal particles and bacterial consortium for effective biodesulphurization. Furthermore, coarse particle greater than +4.60 mm particle sizes were not considered due to stirring difficulties experienced when dealing larger particles. The total sulphur was determined in duplicates using Leco S-628 Elemental analyzer at 1350 °C following ASTM D4239-14 standard.

2.2 Culture characterization

Phylogenetic characterization of cells was performed on individual colonies of bacteria from the 8^{th} -10^{th} tube in the serial dilution preparation. Luria Broth and Plate Count Agar were used for colony development. In preparation for the 16S rRNA sequence identification, the colonies were first classified based on morphology. 16S rRNA genes of the isolates were then amplified by reverse transcriptase-polymerase chain reaction (RT - PCR) using primers pA and pH1. The primer pA corresponds to position 8 - 27 and primer pH1 corresponds to position 1541 - 1522 of the 16S gene (Coenye et al., 1999). The sequences were compared against the GenBank of the National Center for Biotechnology in the United States of America using a basic BLAST search.

2.3 Reaction rates kinetics using AQUASIM 2.0 Software

For a more realistic modelling effort, the reaction rates kinetics was evaluated using the AQUASIM 2.0 software. In AQUASIM 2.0, the mass balance was evaluated numerically by forth order Runge-Kutta method (RK-4). The Monod-like model was used to evaluate the parameter estimations with inhibition coefficient (Haldane model) and without inhibition coefficient (Michaelis-Menten model). The parameters were obtained by minimizing the Chi-square ($\chi 2$) values between the model data and the actual data using a simple method built within AQUASIM (Reichert, 1998).

3. Results and discussions

3.1 Distribution of sulphur forms during biodesulphurization

The relationship between distributions of sulphur forms in coal pre- and post-desulphurization treatment with reference to total sulphur is reported as shown in Table 1. It can be noted that sulphur forms in Waterberg steam coals changed after biodesulphurization treatment. A mathematical expression based on the total sulphur for each sulphur form was developed to establish the effect of biodesulphurization treatment process on Waterberg steam coal. Eq.(1) is used to show how other forms of sulphur relate to the total sulphur.

$$Y = mS_T + c \quad (1)$$

where, Y = form of sulphur, m = distribution factor/gradient, S_T = Total sulphur, c = constant

Table 1: The relationship between sulphur forms in pre- and post-treated Waterberg steam coal

Forms of Sulphur	Pre – Treatment Formula	Post – Treatment Formula
Sulphide sulphur	$S_{IN} = 0.11 \times S_T$	$S_{IN} = 0.14 \times S_T$
Organic sulphur	$S_{ORG} = 0.43 \times S_T$	$S_{ORG} = 0.50 \times S_T$
Pyritic sulphur	$S_{PRY} = 0.44 \times S_T$	$S_{PRY} = 0.311 \times S_T$
Sulphate sulphur	$S_S = 0.02 \times S_T$	$S_S = 0.05 \times S_T$

S_{IN} = Sulphide/ mineral sulphur; S_{PYR} = Pyritic sulphur, S_S = Sulphate sulphur (SS), S_{ORG} = Organic sulphur, S_T= Total sulphur;

The substantial variations are reflected in the increase of the proportions, m or gradient of sulphide sulphur, organic sulphur and sulphate sulphur. The increase of the proportions, m can be attributed to decomposition of pyritic sulphur during desulphurization resulted in forming sulphide sulphur, oxidizing of pyritic sulphur to sulphate sulphur by bacterial consortium and conversion of the sulphide sulphur into organic sulphur. Eq(1) is valid for coal sulphur content and particle size fraction studied.

3.2 Variation of biomass concentration during biodesulphurization

Figure 1 depicts the variations of the biomass concentration and growth curve for cultures studied. The lag phase, an adaptation period, where the bacteria are adjusting to their new conditions was observed. The length of the lag phase generally varies considerably based on how different the conditions are from the conditions that the bacteria came from, as well as the condition of the bacterial cells themselves. The reason for no lag phase can be attributed to bacteria not having to acclimatize to coal as it was isolated from coal. Bacteria can grow very quickly when provided with the right conditions. Bacteria entered the exponential growth phase on Day 0 with viable cells concentration of 44 cells/mL to Day 8 with viable cells concentration of 55 cells/mL until it reached a stationary phase. The stationary phase conditions reached lasted until Day 16th where cells could not grow due to inhibition effect. Therefore, we considered the cultures to be in optimum conditions for use as inocula on Day 10th to Day 16th. At the stationary phase point, the number of new cells being produced is equal to the number of cells dying off or growth has entirely ceased, resulting in a flattening out of growth on the growth curve with viable cells concentration of 55 cells/mL. At some point the bacterial population runs out of an essential nutrient/chemical or its growth is inhibited by its own waste products. Death phase started from the 16th day with viable cells concentration of 55 cells/mL up to 20th Day with viable cells concentration of 41 cells/mL. The steepness of the slope corresponds to how fast cells are losing viability. The current study revealed that in a closed system or batch culture (no food added, no wastes removed) bacteria was still able to grow in a predictable pattern, resulting in a growth curve composed of four distinct phases of growth. However, the lag phase period happed so fast that it couldn't be tracked for the scale of the graph discussed.

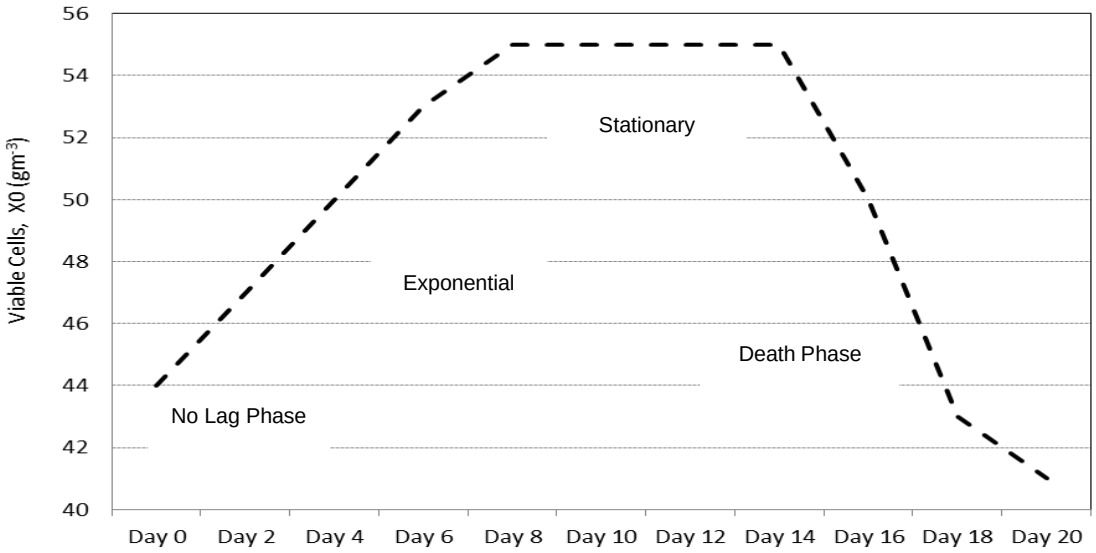

Figure 1: Growth curve for desulphurization process of biomass concentration

3.3 Bacterial Identification

Table 2 shows characterization of bacteria culture using 16S rRNA fingerprint. The strain identification was based on the ± 700 bp partial sequence of the 16S rRNA gene of the organisms. The sequences were compared against the GenBank of the National Centre for Biotechnology in the United States of America using a basic BLAST search. Eight isolates viz: *Bacillus sp, Pseudomonas sp, Pseudomonas aeruginosa, Pseudomonas putida; Pseudomonas stutzeri, Pseudomonas monteilli, Pseudomonas rhizosphaerae and Pseudomonas alcaligenes* were identified after purification of the most dominant colonies. According to Liu et al., 2017, *Pseudomonas sp* in particular *Pseudomonas putida* has been reported for the capability to reduce pyritic sulphur and organic sulphur from the lignite coals. Furthermore, *Pseudomonas putida* bacterium is an effective microbial culture capable to decrease coal organic sulphur.

Table 2: Characterization of bacteria culture using 16S rRNA fingerprint

Number	Result	Query Cover (%)
1	*Pseudomonas putida*	100
2	*Pseudomonas aeruginosa*	100
3	*Pseudomonas sp.*	99
4	*Pseudomonas fluorescens*	100
5	*Bacillus spp.*	99
6	*Pseudomonas stutzeri*	99
7	*Pseudomonas rhizosphaerae*	99
8	*Pseudomonas alcaligenes*	99

3.4 Mass balance around a bioreactor

A general mass balance of the total sulphur around a completely mixed bioreactor is as follows:

$$V\frac{dS}{dt} = Q(S_{in} - S_{out}) + r_s V \quad (2)$$

where S_{in} = Untreated coal total sulphur (wt.%), S_{out} = Treated coal total sulphur (wt.%), r_d = desulphurization rate (MT^{-1}), Q = coal flow rate into the reactor (MT^{-1}), and V = operating volume of the reactor (L^3). Considering batch study (i.e. Q = 1), the left hand derivative approaches zero, i.e. $V\frac{dS}{dt} \rightarrow 0$.Thus, Eq(2) simplifies to:

$$-r_s = \left(\frac{1}{V}\right)(S_{in} - S_{out}) \quad (3)$$

Reaction rate model without inhibition coefficient as described by the Michaelis – Menten substrate utilization rate kinetics was evaluated using the following equation:

$$-r_s = \frac{k_{ms}SX}{K_s+S} \quad (4)$$

where k_{ms} = maximum specific reaction rate coefficient (T^{-1}), K_s = half velocity concentration (ML^{-3}), S = Coal total sulphur content at any time (wt.%) and X = the viable cell concentration in the reactor (ML^{-3}). The reaction rate is substituted into the reactor mass balance as shown in Eq(2). Both organic compounds leached from coal and different trace elements leached out can directly inhibit the microorganisms. However, leached compounds do not necessarily affect the microorganisms in a negative way.

$$V\frac{dS}{dt} = Q(S_{in} - S_{out}) + r_s V$$

$$V\frac{dS}{dt} = Q(S_{in} - S_{out}) + \left(-\frac{k_{ms}SX}{K_s+S}\right)V \quad (5)$$

Which resolves to:

$$\frac{XV}{S_{in} - S_{out}} = \left(\frac{K_s}{k_{ms}}\right)\frac{1}{S_T} + \frac{1}{k_{ms}} \quad (6)$$

The above equation can be solved numerically.

The values of the kinetic parameters, K_s, k_{ms} and K_I in the continuous flow process were determined from the experimental data using Eqs. 5 and 6 and the biological reactor operating conditions shown in Table 3. The details of the numerical calculations for biological reactor kinetic parameters using AQUASIM 2.0 Software. The values are given as recorded in Table 3. The degradation rate coefficient, k_{ms} was determined to be very low compared to the first order maximum reaction rate coefficients, ks. The low value of k_{ms} is a result of the sulphur content of 6 days. The maximum specific reaction rate coefficient in the biological reactor, kms, is lower. This indicates that sulphur reduction happened faster during exponential phase. The high value of K_I also implies that the inhibition was very high which means that the bacteria were probably growing predominantly on sulphur content in coal as a nutrient.

Table 3: Operating conditions for bioreactor

Heading1	-0.85 mm	+1.00 mm	+2.30 mm	+4.60 mm
S_T (wt.%)	1.47	1.32	1.15	1.41
V (L)	1	1	1	1
X_0 (gm^{-3})	32	24	20	17
Cell weight of 1 mL (g)	42×10^{-4}	42×10^{-4}	42×10^{-4}	42×10^{-4}

Since the reactor was operated on batch mode, true steady state conditions could not have been reached. For a more realistic modelling effort, the reaction rates kinetics was evaluated under transient state using the AQUASIM 2.0 software. In AQUASIM 2.0, the mass balance Eqs. 5 and 6 were evaluated numerically by forth order Runge-Kutta method (RK-4). The parameters were obtained by minimizing the Chi-square ($\chi 2$) values between the model data and the actual data using a simple method built within AQUASIM (Reichert, 1998). A model was also developed considering both inhibition coefficient term and without inhibition coefficient term giving the following:

$$S_{in} - S_{out} = V\left(-\frac{k_{ms}C\left(X_0 e^{\left(\frac{Yk_{ms}S}{K_s}-k_d\right)}\right)}{K_s+S}\right) \quad (7)$$

$$S_{in} - S_{out} = V\left(-\frac{k_{ms}C\left(X_0 e^{\left(\frac{Yk_{ms}S}{K_s}-k_d\right)}\right)}{K_s+S+\frac{S^2}{K_I}}\right) \quad (8)$$

Eqs(7) and (8) are quasi second order simple models representing the broad range of biological reactor behaviour of a desulphurization treatment process. Consideration should be given that the developed model may be applied to only wider range of sulphur content range studied and further reassessments are required concentration, S_{in} used in this study. Form Eqs(7) and (8), the average kinetic parameters in the bioreactor were determined for both without inhibition: k_d = 1.65 x 10^{-3} (h^{-1}), K_s = 1.23 x 10^{-4} mgL^{-1}, X_0 = 523 mgL^{-1} and χ^2 = 0.524 and with inhibition, K_I = 371 mgL^{-1} for finer coal particle size.

Table 4: Parameter estimation in bioreactor using AQUASIM Software

Parameters	-0.85 mm	+1.00 mm	+2.30 mm	+4.60 mm
k_d (h^{-1})	1.65 x 10^{-3}	1.83 x 10^{-3}	2.25 x 10^{-3}	3.46 x 10^{-3}
K_I (mgL^{-1})	371	398	403	449
k_{ms} (h^{-1})	4.74 x 10^{-5}	4.66 x 10^{-5}	3.04 x 10^{-5}	3.21 x 10^{-5}
K_s (mgL^{-1})	1.23 x 10^{-4}	2.28 x 10^{-4}	2.84 x 10^{-4}	3.10 x 10^{-4}
X_0 (mgL^{-1})	523	450	413	397
χ^2	0.524	0.450	0.465	0.342

3.5 Overall process efficiencies

To clarify on the biodesulphurization process performance, biodesulphurization efficiency, (η) was calculated based on total sulphur using Eq(9) and the results are recorded in as shown in Figure 2:

$$\eta = \frac{(S_{Untreated\ Coal} - S_{Treated\ Coal})}{S_{Untreated\ Coal}} \times 100 \quad (9)$$

where η is the biodesulphurization efficiency; $S_{Untreated\ coal}$ = the total sulphur of untreated coal; $S_{Treated\ coal}$ = is the total sulphur of treated coal. Figure 2 clearly shows overall process efficiency for – 0.85 mm size, +1.00 mm size, +2.30 mm size and +4.6 mm size is 65.4%, 53.8%, 49.2% and 23.6% respectively.

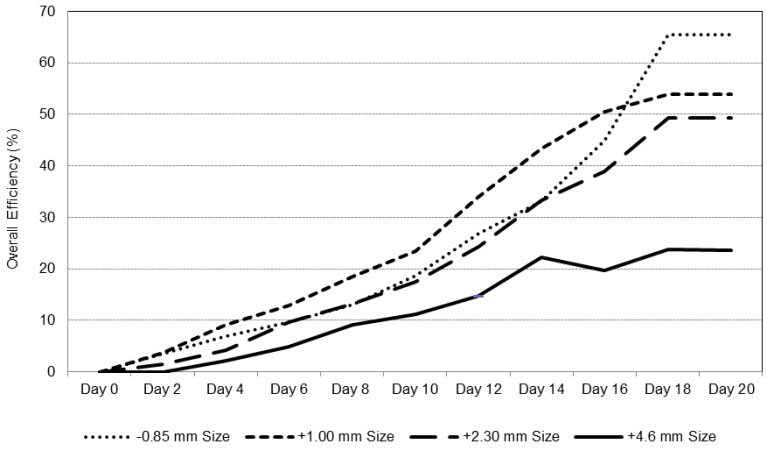

Figure 2: Overall efficiency at various reaction contact time

4. Conclusions

In this study, the Monod-like model was used to evaluate the parameter estimations with inhibition coefficient and without inhibition coefficient. Eight isolates after purification of the most dominant colonies, viz: *Bacillus sp, Pseudomonas sp, Pseudomonas aeruginosa, Pseudomonas putida; Pseudomonas stutzeri, Pseudomonas monteilli, Pseudomonas rhizosphaerae and Pseudomonas alcaligenes*. The model revealed that sulphur reduction process followed quasi-second order kinetics. This study demonstrates the potential of biodesulphurization of Waterberg steam coal as a cleaner and energy effective technology. The biodesulphurization technology, if widely applied in power plants would decrease emissions reduction costs significantly. The complete model data and simulated data have to be experimentally validated under different particle size distribution and it is the intention of the authors to continue in this line.

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