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Performance Evaluation of Microbial Desulphurization of Waterberg Steam Coal as a Pre-Combustion Technique

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The current study evaluates pre-combustion microbial desulphurization of medium – sulphur type coal containing total sulphur (1.45 wt. %) and pyritic sulphur (≥ 0.51 wt. %) in a laboratory scale. Coal samples used in the current study were supplied by one of South African Power Utility, Eskom power station as received from the nearby Waterberg coalfield in Limpopo in South Africa... After a stipulated hydraulic retention time (HRT), the coal samples were filtered, washed, dried and analyzed for total sulphur, ash content and calorific values. The calorific value of the coal significantly improved from 20.42 MJ/Kg to 24.16 MJ/Kg on the 5th day. The process removed up to 72 % of the total sulphur content in the coal samples at an HRT of day 9th. Furthermore, ash content reduced by 16 %. This study provides a novel breakthrough of an alternative microbial desulphurization process of Waterberg steam coal as a pre-treatment technique in order to meet stringent environmental emissions standards for SO_2.

1. Introduction

Environmental impacts associated with the use of coal as a primary source for electricity generation and development of new technologies to mitigate the resulting emissions has received extensive attention recently. Numerous schemes, such as fuel pre-treatment, concurrent burning and adsorption, and flue gas post treatment, i.e., flue gas desulphurization (FGD), have been proposed, Gao et al (2011). Among those schemes, FGD is the most reasonable one from both technological and economic point of views, Gao et al (2011). South African National Power Utility's (Eskom) has made the decision to employ FGD technology for power stations being constructed and where possible to retrofit on the existing power stations (Makgato and Chirwa, 2017a). The FGD technology is used to reduce sulphur emissions in coal-fired power utilities by using pulverized limestone in a spray tower to react with SO_2 in the flue gas and remove sulphur as a solid product (gypsum). However, adding an FGD installation typically increases the total costs of a power plant by one-thirds, Qian and Zhang (1998). To South African National Power Utility's (Eskom), this is excessively expensive as electricity is sold at state regulated low prices. Furthermore, retrofitting of old units is not always possible not only because of the high capital cost involved but also due to space limitations, Efthimiadou et al. (2015). Hence, FGD must be compared with other pre-combustion technologies in order to achieve full environmental assessment compliance in modern power plants to consistently meet the SO_2 emission standards and increase power station availability.

Waterberg steam coal is unique in various aspects relative to other high sulphur coal dominating the literature. A wide variety of physical and chemical methods have been used or proposed for reducing sulphur emissions from coal combustion (Olson and Brinckman, 1986). However, there are problems associated with the existing technology including cost, efficiency, reliability and waste disposal. Microbial processes have the potential to overcome some of these problems. However, limited information is available on the use of biological process in coal desulphurization prior to combustion. The aim of the present study is to evaluate the desulphurization effect of Waterberg coals subjected to biotreatments and to trace the changes that occur with sulphur.

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2. Materials and Methods

2.1 Microorganisms, Media and Chemicals

A mixed culture of sulphur reducing bacteria was collected from nearby stockpiles of newly commissioned South African National Power Utility's (Eskom's) Medupi Power Station as received from nearby Waterberg coalfield (Lephalale, Limpopo Province). The start-up culture was prepared by overnight growth in Luria-Bettani (LB) Agar at 32°C. This culture was used to inoculate the desulphurization reactor. The culture was cultivated in basal mineral medium (BMM) prepared by dissolving in 1 L distilled water: 0.535 g NH_4Cl; 10.744 g $NaH_2PO_4{\cdot}2H_2O$; 2.722 g K_2HPO_4; 0.0493 g $MgSO_4{\cdot}7H_2O$; 0.0114 g $NaSO_4{\cdot}2H_2O$; and 0.0493 g $MgSO_4{\cdot}3H_2O$. The chemicals used in this experiment were obtained at purities higher than 99 % from MERCK Chemicals.

2.2 Microbial desulphurization of coal samples

The desulphurization experiments were conducted in 500 mL continuously stirred Erlenmeyer flask. The flask contained 250 mL of microbial solution and 200 g of – 85 mm coal sample. After the required (Hydraulic Retention Times (HRTs), 20 g of desulphurized coals were sampled, filtered, washed, dried and analyzed for total sulphur, ash content and CV daily as depicted in Figure 1 below:

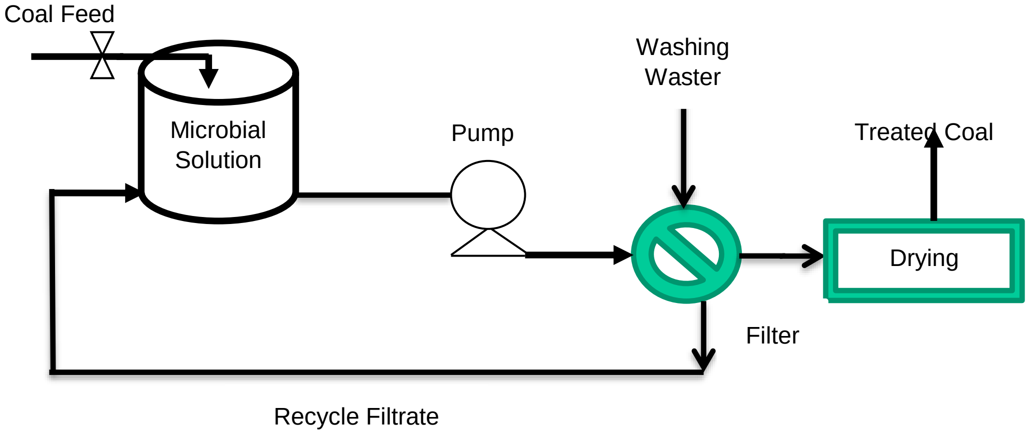

Figure 1: Layout of the experimental set-up

2.3 Determination of ultimate analysis

Ultimate analyses such as Carbon (C), Hydrogen (H) and Nitrogen (N) were determined using LECO-932 CHNS Analyzer following ISO 12902:2001 standard procedure.

2.4 Total Sulphur Analysis

The total sulphur was determined in duplicates using Leco S-628 Elemental analyzer at 1,350 °C following ASTM D4239-14 standard procedure.

2.5 Calorific value measurement

Coal samples were burnt in a bomb calorimeter and the calorific value (CV) was measured following ISO 1928, 2009 method.

3. Results and Discussions

3.1 The effect of biodesulphurization treatment on ash content

The results presented in Table 1 shows the effect of microbial treatment on coal ash content. It is evident from Table 1 that microbial treatment has a big effect on the reduction of coal ash content. Ash content decrease was found to increase with hydraulic retention time (HRT). The overall decrease in ash content from Day 0 to Day 10^{th} is about 16 %. No further ash content reduction beyond Day 7^{th} as the systems reached *quasi* steady-state. The present study's findings indicate that coal ash content could be reduced further due to desulphurization process. This is more desirable as more ash content in coal requires frequent disposal in ash dam which pose environmental challenges.

Table 1: Treated coal ash content over various HRTs

Time	Sample 1 Ash content (wt. %)	Sample 2 Ash content (wt. %)
Day 0	31.0	31.0
Day 1	31.0	31.0
Day 2	30.9	30.8
Day 3	30.8	30.6
Day 4	30.8	30.2
Day 5	29.6	28.8
Day 6	28.5	27.9
Day 7	26.1	26.3
Day 8	26.0	26.2
Day 9	26.1	26.2
Day 10	26.0	26.1

Bacterial Identification

Phylogenetic characterization of cells was performed on individual colonies of bacteria from the 8^{th} -10^{th} tube in the serial dilution preparation. LB and PC agar was used for colony development. In preparation for the 16S rRNA sequence identification, the colonies were first classified based on morphology. Table 2 shows Blast result with max ID of these species.

Table 2: Analysis of coal samples

Number	Result	Query Cover (%)
1	*Pseudomonas Monteilli*	100
2	*Bacillus Aryabhattai*	100
3	*Pseudomonas Aeruginosa*	100
4	*Bacillus Cerus*	100

A possible identification for the 10 isolates (*Pseudomonas monteilli* x 4; *Pseudomonas aeruginosa* x 3; *Bacillus aryabhattai* x 2 abd Bacillus cerus x 1) have been obtained after purification of the most dominant colonies. 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 Center for Biotechnology in the United States of America using a basic BLAST search. *Pseudomonas aeruginosa* has been extensively studies in the degradation of chlorophenols and other polynuclear aromatic compounds, Gaofeng et al. (2004) while other species such as *Bacillus* strains are capable of reducing sulphur content in coal samples.

The effect of calorific value at various HRTs

An important property, which indicates the useful energy content of a coal and thereby its value as a fuel, is its CV (also known as heat of combustion), which is defined as the amount of heat evolved when a unit weight of fuel is burnt completely, and the combustion products cooled to a standard temperature of 298 K, Patel et al. (2007). In order to observe the effect of coal samples CV at various HRTs, samples were taken in duplicates and the results are as depicted in Figure 2. The CV of the coal significantly increased from 20.42 MJ/Kg at Day 0 to 24.16 MJ/Kg on the 5^{th} day, decreased on the 6^{th} day to the 8^{th} day to almost the original value and increased on the 9^{th} day and 10^{th} day to 20.9 MJ/Kg. The results indicate a HRT of 5^{th} day to be the best highest CV value. The present study's findings indicate that the coal CV could be improved due to desulphurization process. According to Makgato and Chirwa (2017a), the increase and decrease of CV can be attributed to changes in carbon, hydrogen, sulphur content, and ash content due to desulphurization process as per Equation 1:

$$CV = 0.472C \times 1.30H \times 0.190S + 0.107A - 7.52 \quad (1)$$

where: C = Carbon, H = Hydrogen, S = Sulphur, and A = Ash.

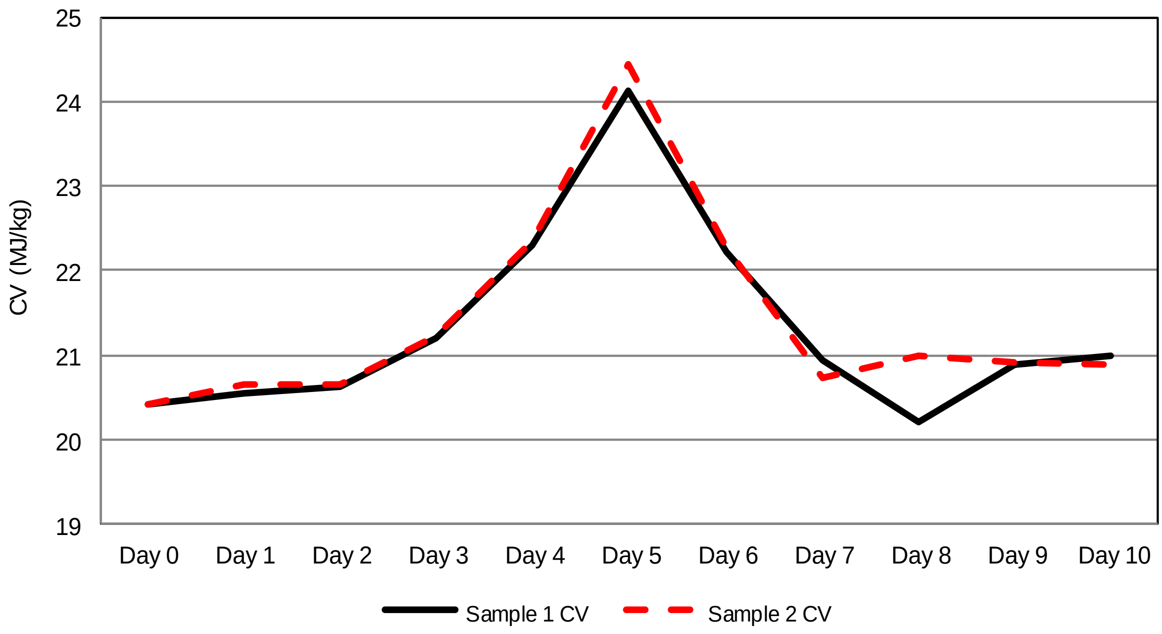

Figure 2: Calorific value at various HRTs

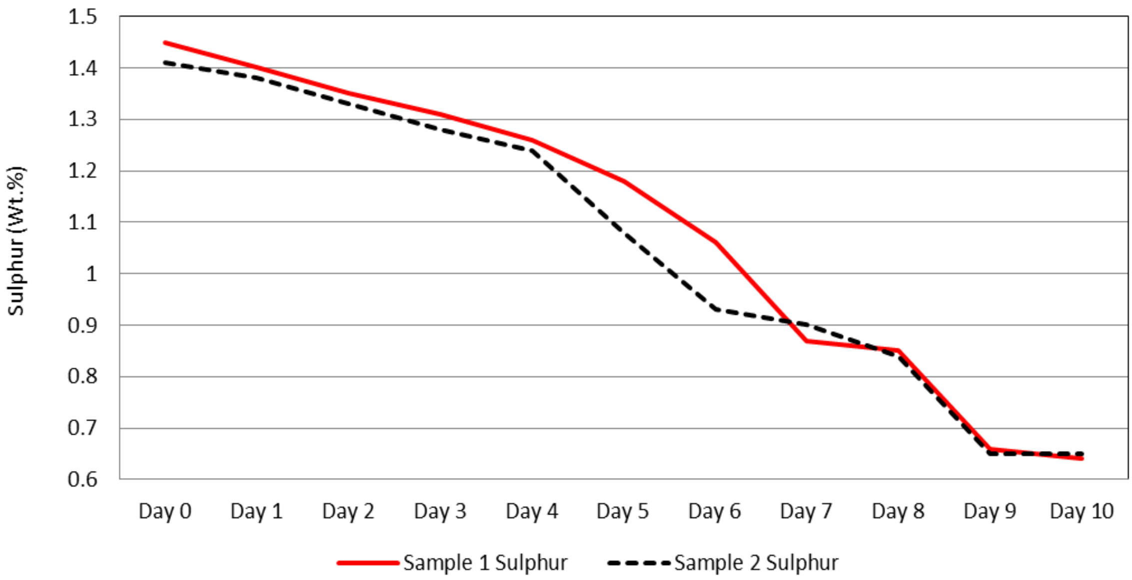

Figure 3: Variation of sulphur content with HRTs

3.2 Performance evaluation of coal slurry reactor at various HRTs

The performance evaluation of coal slurry reactor at various Hydraulic Retention Times (HRTs) is presented in Figure 3. The coal slurry reactor was operated at HRTs ranging from 0 to 10 days corresponding to sulphur content of 1.45 to 0.41 respectively. The results indicate that an HRT of 9^{th} and 10^{th} day is observed to be the best lowest sulphur content received which resulted in 72 percent removal of sulphur from Waterberg coal. Pandey et al., (2005) have cited that the optimal HRT for slurry reactor system for microbial desulphurization of coal containing pyrite in the ranges of 9 – 28 days. Therefore, the present study's findings indicate that the coal slurry reactor operated for desulphurization of power generation coal as a feasible pre-combustion technique and showed better efficiency as compared to the reports cited in earlier literature by Pandey et al. (2005). Direct mechanisms of desulphurization could be summarized as follow: the microorganisms firstly attached themselves to the coal particles, which in turn solubilize the coal samples. This attachment, which is part of the overall process, is known to be fast (Weerasekara et al., 2008). The attachment normally takes place in specific locations in the coal particle such as cracks, voids, defects, etc. which are uniform in size and distributed throughout the volume of the coal samples. Following the attachment, the desulphurization process can therefore be assumed to take place.

3.3 Total Sulphur Removal Calculations

Total sulphur removal calculations per HRTs can be calculated using Eq(2) below:

$$\eta = \frac{S_{Feed} - S_{Treated}}{S_{Feed}} \times 100 \qquad (2)$$

where S_{Feed} is total sulphur in the feed; $S_{Treated}$ is total sulphur the treated coal.
The value of the desulphurization process efficiency per HRTs is reported in Table 3. It is clear from these total sulphur calculations that the process efficiency of up to 72 % is obtained which is more desirable. Earlier studies by Makgato and Chirwa (2017b) indicated that for any pre-combustion technique required to be competitive with post combustion technique, FGD then overall pre-combustion process efficiency (η) of greater than 80 % is required in order to meet the South African minimum emissions standards for sulphur target of 500 mg/Nm^3. Although, reduction of sulphur content from coals prior to combustion would decrease SO_2 emissions, there is further work to be undertaken in prolonging the HRTs by increasing the reactor size as samples required for analysis cannot be reduced. In addition, the optimum HRTs should be established and indicate if there is a need for recycling microbial treated coal (if any) and up-scaling this process for commercial purposes. Furthermore, there is a need to quantify sulphur forms mainly affected by the desulphurization process compared with both physical and chemicals processes.

Table 3: Process efficiency over various HRTs

Time	Sample 1 η	Sample 2 η
Day 0	0	0
Day 1	3.6	2.1
Day 2	3.7	3.8
Day 3	3.1	3.1
Day 4	3.8	3.9
Day 5	17	23
Day 6	27	34
Day 7	40	36
Day 8	41	40
Day 9	72	71
Day 10	72	72

To meet the South African minimum emissions standards for sulphur target of 3,500 mg/Nm^3, approximately 17 – 23 % of the total sulphur in the coal must be removed. Figure 3 depicts SO_2 emissions for coal samples studied. It is evident from Figure 3 that SO_2 concentration decreases linearly from 3692 mg/Nm^3 at Day 0 to 2,197 at Day 8 HRTs as sulphur content in the coal samples decreases. This implies that volumes of emission of sulphur compounds are directly proportional to amounts of sulphur content present in the parent coal. The sampling was limited to volume of coal required for coal analyses as such bigger reactor is required to extend the HRTs.

4. Conclusions

The desulphurization process of medium sulphur Waterberg steam coal using micro-organisms, naturally present in coal, have the ability to reduce its sulphur content, ash content and improve CV. Sulphur content reduced by 72 %, ash content reduced by 16 % and CV improved by 22 %. Approximately 10 isolates were obtained after purification of the most dominant colonies. Desulphurized coal would not require the use of FGD and coal users would have no sulphur wastes to dispose of. This finding is the first step in the development of microbial desulphurization technique as a pre-combustion technology for South African power generation industry where SO_2 emissions have been legislated. There is further work to be undertaken in comparing costs of microbial desulphurization versus FGD. It is the intention of the author to continue further in this regard.

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