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# Desulphurization of Medium Sulphur Waterberg Steam Coal in a Batch Operated Scale: Microbial Solution

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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. Coal samples were size fractioned using 13.2, 9.5, 8.0, 6.3, 5.6, 4.7, 2.36, 2.00, 1.00, 0.85 mm and below using automatic screens shaker. Coal sample containing particle size in the range of – 0.85 mm was used in the experiments with bacteria isolated from the native coal mine site. After a stipulated hydraulic retention time (HRT), the coal samples were filtered, washed, dried and used for total sulphur and calorific value analysis. 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 41% of the total sulphur content in the coal samples at a HRT of 8 days. This study provides a novel breakthrough of an alternative microbial desulphurization process of Waterberg steam coal as a further pre-treatment technique in order to meet stringent environmental emissions standards for $SO_2$.

## 1. Introduction

Coal is considered as one of the major energy sources in South Africa. Ninety-one percent (91%) of the electricity generated in South Africa is based on coal combustion in steam-turbine driven power plants (IEA, 2014). In the process of electricity generation, coal is transformed into ash and gases, which cause numerous environmental problems like acid rain. 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. South African National Power Utility's (Eskom) has made the decision to employ flue gas desulphurization (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 pulverised limestone in a spray tower to react with $SO_2$ in the flue gas and remove sulphur as a solid product (gypsum). In spite of the good performance of the FGD technology thus far, the process produces effluent with high concentrations of the cationic and anionic impurities as well as heavy metals. However, power stations that have already passed their half-life will need serious review in light of what is affordable. Therefore, FGD must be compared with other pre-combustion techniques that can enable power station comply with the $SO_2$ emission standards and increase power station availability.

There are effective technologies to remove sulphur after or during combustion, but there is no technology for removing sufficient sulphur before combustion to meet the minimum emissions standards. One method of minimising the later problem is to reduce the amount of pollutant elements in coal, such as sulphur, before it is burnt. This will reduce the amount of sulphur-derived gases like SOx formation and acid formation after those gases leaving the boiler utility (Weerasekara et al., 2008). 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 these technologies including cost, efficiency, reliability, destroying coal properties, energy intensive and waste disposal. Furthermore, chemicals employed for desulphurization may sometimes be hazardous to the environment and lethal to the humans for their explosive and toxic nature, Saikia et al (2016). The use of bacteria to remove sulphur could be financially viable because

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no external energy required for the process other than pumping the bacteria rich solution to the coal. Several studies were published about biological desulfurization of coal. The research on microbial desulphurization of coal has concentrated on the removal of pyritic sulphur using *Thiobacillus ferrooxidans* or a mixed culture of *T. ferrooxidans* and *T. thiooxidans* (Kargi, 1982) which the pyrite could be effectively removed by physical processes. Waterberg coal is unique in various aspects relative to other high sulphur coal dominating the literature. Therefore, limited information is available on the use of biological process in coal desulphurization prior to combustion. The feasibility of microbial processes to overcome some of the challenges already mentioned with the use of either physical and chemical techniques have not yet been completed to assess its feasibility as a pre-combustion technique. The aim of the present study is to evaluate the microbial desulphurization process and to trace the changes that occur with coal key properties during desulphurization.

## 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. LB Agar was prepared by adding 20 g of agar powders in 1000 mL of distilled water. LB Agar was autoclaved for 15 minutes and allowed to cool to 45°C before use.

Two coal samples of –0.85 mm particle size were used for microbial desulphurization experiments in a Continuously Stirred Tank Reactor (CSTR). The sulphur compounds present in coal has already been classified in earlier studies by Makgato and Chirwa (2017a). In summary, two major categories are pyritic sulphur (0.51 wt.%) and organic sulphur (0.49 wt.%) which accounted for the bulk of the total sulphur in coal. Analysis of coal sample used is detailed on Table 1.

*Table 1: Analysis of coal samples*

| Analysis | Value |
|---|---|
| *Proximate Analysis (wt.% as received)* | |
| Moisture | 2.50 |
| Ash | 31.0 |
| Volatile Matter | 24.0 |
| Fixed Carbon | 38.5 |
| *Ultimate Analysis (wt.% on dry-basis)* | |
| Carbon | 55.6 |
| Hydrogen | 3.07 |
| Sulphur | 1.45 |
| Nitrogen | 1.14 |
| Oxygen (By difference) | |
| Calorific value (MJ/Kg) | 20.42 |

### 2.2 Source of microorganisms

Collected coal samples were used for bacterial enrichment through subsequent transfer on mineral salt medium. 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 $MgSO_4{\cdot}3H_2O$. Aerobic cultures were grown in 1 L Erlenmeyer flasks covered with cotton plugs, in suspension by agitation at 120 rpm and 28 ± 2 °C for 48 hrs using a Labcon SPL-MP 15 Lateral Shaker (Labcon Laboratory Services, South Africa).

### 2.3 Microbial desulphurization of coal samples

The experiments were carried out for microbial desulphurization of the two different coal samples immediately after their collection. The desulphurization experiments were conducted in 500 mL Erlenmeyer flask. The flask contained 250 mL of microbial solution and 200 g of coal sample. After the required (Hydraulic Retention Times (HRTs), 20 g of desulphurized coals were sampled, filtered, washed, dried and analysed for total sulphur and CV.

### 2.4 Determination of ultimate analysis

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

### 2.5 Total Sulphur Analysis

The total sulphur was determined in duplicates using Leco S-628 Elemental analyser at 1350 °C following ASTM D4239-14 standard procedure.

### 2.6 Calorific value measurement

Coal samples were burnt in a bomb calorimeter and the 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 2 shows the effect of microbial treatment on coal ash content. It is evident from this Table that microbial treatment has a big effect on the reduction of coal ash content. Ash content decrease was found to increase with reaction time. The overall decrease in ash content from Day 0 to Day 8$^{th}$ is about 16%. No further samples could be taken in order to further observe the effect of HRTs on coal ash content due to limited samples available as a result of samples requirements for ash analysis. The present study's preliminary findings indicate that the coal ash content could be improved due to desulphurization process. However, more experiments are required to establish the optimum conditions for maximum ash content reduction.

*Table 2: Treated coal ash content over various HRTs*

| Time | Sample 1 Ash content (wt.%) | %Ash Removed | Sample 2 Ash content (wt.%) | %Ash Removed |
|---|---|---|---|---|
| Day 0 | 31.0 | 0 | 31.0 | 0 |
| Day 5 | 30.8 | 0.65 | 30.2 | 2.58 |
| Day 6 | 29.6 | 3.90 | 28.8 | 4.64 |
| Day 7 | 27.5 | 7.09 | 27.9 | 3.13 |
| Day 8 | 26.1 | 5.09 | 26.3 | 5.73 |

### 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 1. The coal slurry reactor was operated at HRTs ranging from 0 to 8 days corresponding to sulphur content of 1.45 to 0.84 respectively. The results indicate that a HRT of 8 day is observed to be the best lowest sulphur content received which resulted in 40 percent removal of sulphur from the coal. From 7$^{th}$ day to 8$^{th}$ day indicated the lowest removal rate as opposed to earlier days. No information is available for further increase in the HRT beyond 8$^{th}$ day could not take place as all feed samples were depleted due to the amount of coal samples required for analysis. 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 literature (Pandey et al., 2005). Direct mechanisms of desulphurization could be summarised as follow: the microorganisms firstly attached themselves to the coal particles, which in turn solubilise the minerals. 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 be assumed to take place.

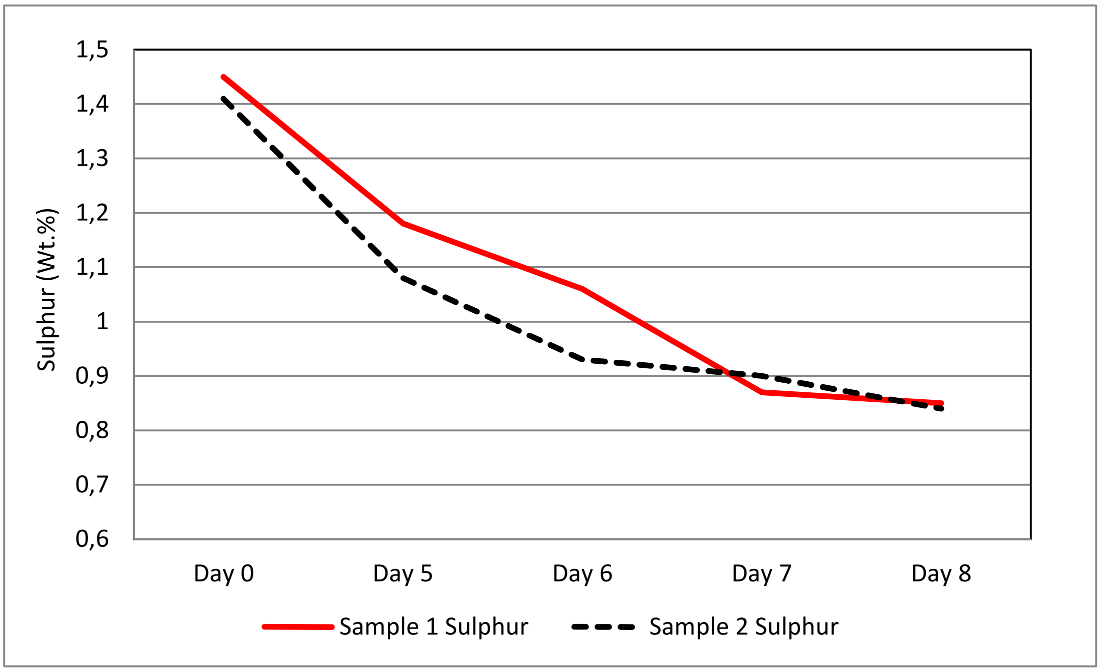


*Figure 1: Variation of sulphur content with HRTs*

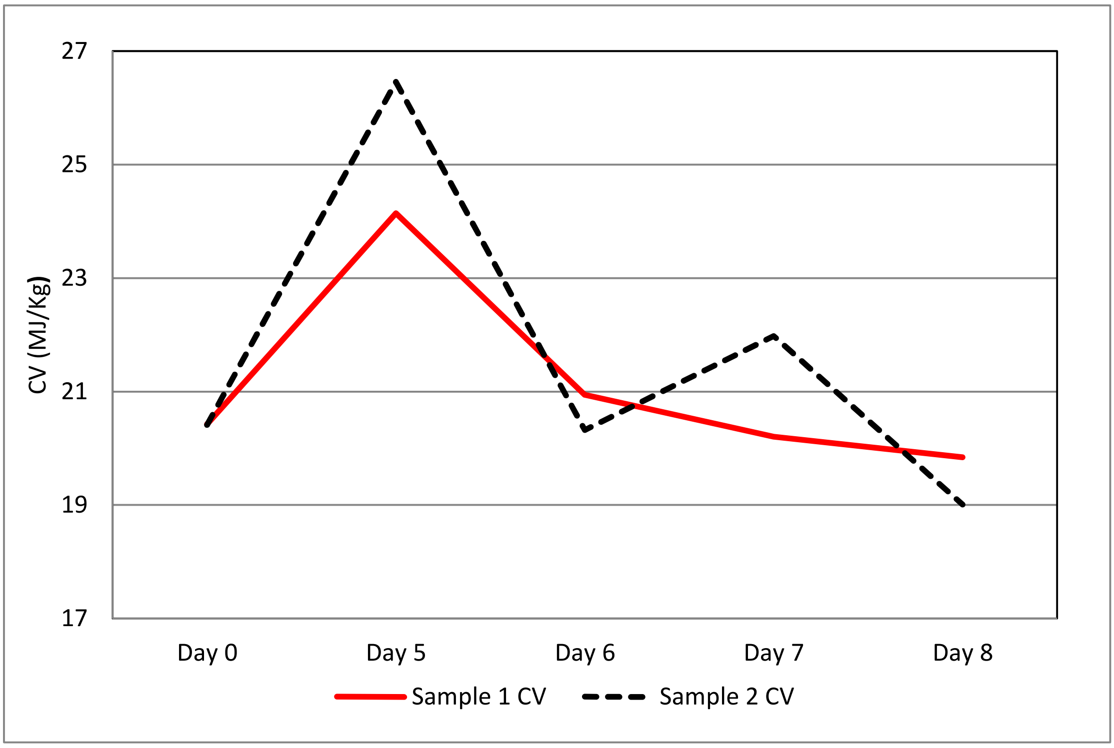


*Figure 2: Calorific value at various HRTs*

**3.3 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 calorific value (also known as heat of combustion), which is defined as the amount of heat evolved when a unit weight of the 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 calorific value (CV) at various HRTs, samples were taken and the results are as reported in Figure 2. The calorific value of the coal significantly increased from 20.42 MJ/Kg to 24.16 MJ/Kg on the 5th day, decreased on the 6th day and increased on the 7th day and lastly decreased to 19.1 MJ/Kg on the 8th day. The results indicate a HRT of 5th day to be the best highest calorific value resulting in an increase from 20 MJ/Kg to 24 MJ/Kg with only a small decrease in calorific value at days 6th and 8th. Day 5th indicate a better improved CV due to pre-combustion desulphurization technique employed. The increase in the calorific values for day 0 to day 5 was influenced by desulphurization process of coal samples. However, as HRTs, increases beyond the 5th day, CV decreased slight within the acceptable limits. Similar to the performance evaluation of coal slurry reactor, no further samples could be taken in order to further observe the effect of HRTs on CV due to limited samples available as a result of samples requirements for analysis. The present study's findings indicate that the coal CV could be improved due to desulphurization process. However, the details of samples requirements should be factored in the reactor, to determine the volume of CSTR required establishing the maximum desulphurization efficiency of the Waterberg steam coal.

### 3.4 Total Sulphur Removal Calculations

Total sulphur removal calculations per HRTs can be calculated using Equation (1) below:

$$\eta = \frac{S_{Feed} - S_{Treated}}{S_{Feed}} \times 100 \quad (1)$$

where SFeed is total sulphur in the feed; STreated 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 41% is obtained. 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 ($\eta$) of greater than 80% is required which the current process obtained only half. Although, reduction of sulphur content from coals prior to combustion would decrease SO2 emissions, there is further work to be undertaken in prolonging the HRTs by increasing the reactor size as samples required form 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 $\eta$ | Sample 2 $\eta$ |
|---|---|---|
| Day 0 | 0 | 0 |
| Day 5 | 17 | 23 |
| Day 6 | 27 | 34 |
| Day 7 | 40 | 36 |
| Day 8 | 41 | 40 |

## 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. The study was carried out in batch operated scale. The result from this study indicated that the parent coal key properties such as CV, ash content and sulphur content was are affected by further microbial desulphurization of already beneficiated steam coal. The study has shown that significant sulphur reduction can be achieved by further treatment employing pre-combustion technique. It would be possible to reduce medium type Waterberg coal to low sulphur type. This finding is a first steps 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. Power plants users could benefit from the adoption microbial pre-treatment technology for $SO_2$ emissions compliance. Significantly, more research is needed to establish the capabilities, limitations and optimum conditions for this coal treatment process. It must be stated that, whilst the objective this research was accomplished, there is further work to be undertaken in characterization and microbial culture monitoring throughout the desulphurization process, investigate the effect of particle size variation on process efficiency as well as establishing baseline information for up-scaling this process for commercial purposes. It is the intention of the authors to continue further in this regard.

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