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Biodesulphurization of Turkish lignite by *Leptospirillum ferriphilum*: Effect of ferrous iron, Span-80 and ultrasonication

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ABSTRACT

Coal has been serving as a profuse source of energy since centuries and several attempts are being made to reduce sulphur emission levels from coal. Recently, pretreatment techniques such as ultrasonication and utilization of surfactants as additives have surfaced aiming at improving the biodesulphurization of coal. In the present study, biodesulphurization of Turkish lignite was studied for the first time using *Leptospirillum ferriphilum.* Attempts have been made to study the biodesulphurization aspects of the lignite sample where the effect of Fe^{2+} iron, surfactant Span 80 and ultrasonication were studied under shake flask conditions. The study indicated Fe^{2+} to be an essential component in the growth media for improving biodesulphurization performance (with 56.2% total sulphur removal). Span 80 (0.05% v/v) marginally enhanced the biodesulphurization of the lignite sample (nearly 61% of total sulphur removal). The carbon content in the lignite sample increased following biodesulphurization. Ultrasonication of the lignite sample, on the other hand, did not yield significant sulphur removal when compared to the effect of Span 80. About 57.6% of total sulphur could be removed from the sample when ultrasonicated for 60 min. Mineralogical characterization along with thermal analysis of the samples pre and post biodesulphurization provided more information on different phases present in coal and the effect of microbial treatment on them.

1. Introduction

Coal is one of the most widely used resources of energy and finds its application in several sectors. However, presence of certain undesired compounds in coal delimits its use in some areas. Mostly, combustion of sulphur containing compounds made up of various organic and inorganically bound sulphur release sulphur oxides into the atmosphere, which is responsible for certain environmental and health problems (Soleimani et al., 2007). Therefore, the past few years have been witnessing a strict regulation by governmental bodies to lower the sulphur emission levels from various coal power plants and industries. The urge to reduce sulphur levels in coal has led to the search for an apt technique for desulphurization of coal. In this regard, the biodesulphurization method has been gaining momentum in the past few years due to its several advantages over the physicochemical techniques of sulphur removal (Mishra et al., 2014).

The percentage of sulphur in coal varies according to the rank of coal and reports state that lignite contains a higher percentage of pyritic sulphur (Acharya et al., 2001; Mishra et al., 2015). Turkey comprises of vast reserves of lignite, which is primarily used for electricity production, steel manufacturing and in cement industries (Yılmaz and Uslu, 2007). It contributes to nearly 42.5% of the overall energy production in Turkey (Yuksel and Kaygusuz, 2011). There are about 142 lignite fields in Turkey, which amount to 10.2 billion tons (Bt). Taking into consideration the abundance of lignite reserves of Turkey, the Turkish government has been focusing more towards utilization of this resource instead of natural gas and other imported energy sources. Conversely, the high sulphur content of Turkish lignite samples delimits its efficiency and thus its removal is essential prior to its application in several sectors. Attempts have been made in this regard using some heterotrophs and acidophilic stains. Recent studies by Aytar et al. (2014) on the Turkish lignites obtained from the Mihaliccik region of Turkey revealed a total desulphurization of 52% using fungus *Alternaria* sp. Cf1. In addition, certain acidophilic strains such as *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* have also been used for the biodesulphurization of Cayirhan lignites, which resulted in a maximum sulphur removal of 78.2% (Gürü et al., 2006). In general, biodesulphurization of coal has also been reported using several bacterial and

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fungal strains such as *Sinomonas flava* XL4, *Sulpholobus acidocaldarius*, *Sulpholobus brierleyi*, *Pseudomonas aeruginosa*, *Pseudomonas putida*, *Beggiatoa*, *Rhodococcus* sp., *Fusarium oxysporum*, *Aspergillus niger* and *Exophiala spinifera* (Etemadzadeh et al., 2016; Liu et al., 2015; Mishra et al., 2016, 2017).

Some recent investigations on enhancement of biodesulphurization activity have highlighted the application of surfactants and pretreatment techniques for improving sulphur removal efficiency (Mishra et al., 2016 and references therein). Surfactants are amphiphilic compounds, which enhance the rate of desulphurization by increasing the mass transfer of the system, while pretreatment techniques like ultrasonication and microwave irradiation create cavitation and selective heating respectively, which in turn improves the sulphur removal efficiency (Mishra et al., 2016 and references therein). Owing to the catalytic effect of surfactants and the role of pretreatment techniques towards improving the biodesulphurization of coal, the present study was designed to make a comparative analysis on the effect of non-ionic surfactant Span-80 and ultrasonication on the biodesulphurization of Turkish lignite in presence of *Leptospirillum ferriphilum*. It is very important to note that the literature is very scanty on the desulphurization of lignite by *Leptospirillum ferriphilum* and also on the effects of surfactant and/or ultrasonication on biodesulphurization in acidophilic biosystems. Therefore, the present investigation primarily focuses on biodesulphurization ability of a pure strain of *Leptospirillum ferriphilum* for Turkish lignite sample with insights into the changes in physicochemical conditions of the biodesulphurization system in presence and absence of Span-80 and/or ultrasonication.

2. Materials and methods

2.1. Coal sample

The "as received" coal sample (lignite) used in the present study was obtained from TKI Çan Linyit İşletmesi Md., Can, Canakkale, Turkey. The sample (+10 cm) was subjected to conventional coning and quartering method and a representative of it was used for grinding. The ground sample was sieved to obtain a final size fraction of −75 + 45 μm prior to its use in biodesulphurization experiments.

2.2. Microbial growth and adaptation

Acidophilic strain, *Leptospirillum ferriphilum* DSM 14647 (*L. ferriphilum*) used in the present study was obtained from culture collection center DSMZ, Germany. The strain was activated in DSMZ standard recommended media having the following chemical composition:

(a) Solution A (mg/950 mL): $(NH_4)_2SO_4$ – 132, $MgCl_2 \times 6H_2O$ – 53, KH_2PO_4 – 27, $CaCl_2 \times 2H_2O$ – 147 and Trace element solution – 1 mL. The Trace element solution had the chemical composition (mg/L): $MnCl_2 \times 2H_2O$ – 62, $ZnCl_2$ – 68, $CoCl_2 \times 6H_2O$ – 64, H_3BO_3 – 31, Na_2MoO_4 – 10 and $CuCl_2 \times 2H_2O$ – 67.
(b) Solution B: 20 g $FeSO_4 \times 7H_2O$ in 50 mL of 0.25 N H_2SO_4.

The pH of Solution A was adjusted to 1.8 and that of Solution B to 1.2, using H_2SO_4, prior to autoclaving. Solution A and B were autoclaved separately at 112 °C for 30 min and then mixed after sterilization. The final pH of the growth medium was maintained at1.8. Adaptation is considered as a unique biotechnological feature of acidophiles that improves their ability to leach metal values from ores or industrial wastes (desulphurization in this case) (Panda et al., 2015a). Following complete iron oxidation, the active culture was adapted to 2% (*w/v*) of lignite sample in the same growth medium and the coal adapted culture was further used for biodesulphurization experiments.

2.3. Biodesulphurization experiments

The biodesulphurization ability of *L. ferriphilum* for Turkish Lignite (herein referred to as "TL" throughout the text) was studied in shake flasks. For this study, three different sets of experiments were designed. In the first set, effect of ferrous iron (in the bacterial growth media) on biodesulphurization of TL sample was studied. Taking the results of the first set into consideration, the second and third sets of experiments were designed. The second set aimed at studying the effect of surfactant on biodesulphurization of TL sample and the third set was aimed at studying the effect of ultrasonication as a pretreatment technique.

For each set, the experiments were performed in 250 mL shake flasks. Initially, all the experimental flasks contained 90 mL of recommended media (based on the experimental requirement as discussed in the sections below) and 5% (*w/v*) of TL sample that were autoclaved prior to inoculum additions. Following sterilization, 10 mL of the active adapted culture of *L. ferriphilum* was added to each experimental flask in order to maintain a total working volume of 100 mL with a final pH of 1.8. Under similar conditions, a control set of experiments (without bacterial inoculum) were simultaneously carried out in 250 mL flasks containing 100 mL of the DSMZ recommended media. The flasks containing ferrous sulphate in medium was designated as $\text{Control}^{(+)}$ and the other without ferrous sulphate was designated as $\text{Control}^{(-)}$. All the flasks under study were maintained at 32 °C and operated at 150 rpm in an orbital shaker incubator (GALLENKAMP Orbital Shaker – Incubator) for 21 days.

2.3.1. Set 1 – Effect of ferrous iron

In this set, biodesulphurization of the lignite sample was studied in presence and absence of ferrous sulphate in the DSMZ media. The growth media (see Section 2.2) with ferrous sulphate was designated as $GM^{(+)}$, while that devoid of it was designated as $GM^{(-)}$. All other constituents of the media remained same. 5 g of the TL sample were added in separate flasks containing 90 mL of $GM^{(+)}$ and $GM^{(-)}$ and were autoclaved prior to inoculum addition (10 mL). The final pH in both the flasks was adjusted to 1.8 with H_2SO_4.

2.3.2. Set 2 – Effect of surfactant

In this set, a non-ionic surfactant – Span80 was used. In order to optimize the dose, the concentration of Span-80 was varied as (v/v): 0.02%, 0.05%, 0.08%, 0.1%, 0.15%, 0.2%, 0.5%, 1% and 2% in the respective experimental flasks containing $GM^{(+)}$ growth media. Simultaneously, a control experiment was performed for this set in order to directly observe the biodesulphurization efficiency of *L. ferriphilum* towards lignite sample. For the control experiment, no surfactant was added to sterile leaching medium; however, all the other conditions remained same.

2.3.3. Set 3 – Effect of ultrasonication

For the second set, 5 g each of the coal sample (−75 + 45 μm size) was initially sonicated in different 250 mL conical flasks containing 90 mL of the pH – 1.8 sterile $GM^{(+)}$ growth medium. The flasks were sonicated for 10, 20, 30, 40 and 60 min respectively in a sonicator (Wise Clean) having 40 KHz Frequency and 540 Wattage. The inner diameter of the sonicator was 290 × 240 × 50 cm (W × L × H) and the outer diameter was 393 × 265 × 307 cm (W × L × H). The water bath of the sonicator had transducers fixed to its bottom. Prior to sonication, the water bath was filled with distilled water (dH_2O), which builds the medium for propagation of ultrasound. Proper care was taken to maintain the position of the flask at the centre of the water bath, every time the sonication was performed. The purpose was to avoid errors due to spatial variation in the water bath. A constant temperature was maintained in the water bath by changing the water at routine time intervals (Bhasarkar et al., 2015). Following ultrasonication for the specified time, 10 mL of the active adapted *L. ferriphilum* inoculum was added to respective flasks containing the growth medium and the