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Desulfurization of Tabas coal using chemical (Meyers, Molten caustic leaching) and biological (bioleaching) methods

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ABSTRACT

From an economic, technological, and environmental perspective, sulfur removal from coal resources has received increased attention in recent years. The present work investigates the ability of chemical (Meyers and Molten caustic leaching (MCL)) and biological methods for the desulfurization of Tabas coal. Accordingly, in the Meyer process, at 1 M ferric sulfate concentration, during 90 minutes at 90 ° C, 61.78 % of ash and 82% of pyrite, and 51.35% of total sulfur were removed from Tabas coal, respectively. The MCL method was also investigated. Hence, based on the MCL experimental condition of caustic soda /coal ratio of 2, leaching time of 60 minutes, and constant temperature of 180 ° C, 71.82 % of ash, 88% of pyrite sulfur, and 57.85% of total sulfur content were removed from Tabas coal, respectively. Furthermore, biodesulfurization of Tabas coal was conducted using a mixed culture of acidophilic iron- and sulfur-oxidizing mesophilic bacteria. The effect of time, bacterial medium, solid/liquid (S/L) %, and the absence of bacteria were investigated, and based on the results, time was the most significant parameter. Accordingly, 68.98% of ash, 92% of pyrite sulfur, and 72.43% of total sulfur were removed from Tabas coal with 20% v/v bacterial inoculum during 20 days, respectively.

Keywords: *Tabas coal, Coal desulfurization, Biodesulfurization, Chemical desulfurization, Ash removal, Bioleaching.*

1. Introduction

Coal is a significant portion of natural energy resources, accounting for 66.8% of recoverable fossil fuel resources [1]. Tabas coal is the biggest Iran coal reserve and has the largest proportion (60-70%) in Iran's coking and steel industry. Sulfur removal from coal is one of the most challenging issues. Organic sulfur, pyrite sulfur, and sulfate sulfur are the primary forms of sulfur in coal [2, 3]. Organic sulfur removal from coal is difficult, whereas inorganic sulfur can be easily removed from coal [4]. The majority of inorganic sulfur is found in separate mineral phases as pyrite or marcasite; the rest is found as sulfates, most often gypsum or iron sulfate [5]. Organic sulfur is found in thiols, sulfides, disulfides, and heterocyclic thiophene molecules directly attached to the organic coal matrix [6].

Sulfur removal from coal has been studied using a variety of techniques in the literature, including physical, chemical, physicochemical, and biological processes [7–10]. Magnetic separation, flotation, and oil agglomeration are examples of physical and Physico-chemical processes for the desulfurization of coal. Desulfurization procedures can remove inorganic sulfur and ash-forming minerals [11]. The Meyers process was used to remove the majority of southeastern Anatolian asphaltite's pyritic and sulfate sulfur [12]. Molten caustic leaching (MCL) also has been used to investigate the chemical cleaning of solid fuels [13]. During molten caustic leaching (MCL), caustic reacts with minerals and organosulfur compounds in the fuel to produce water-soluble alkali metal salts and remove ash pyrite and organic sulfur from coal [14]. Biological desulfurization, using a variety of microorganisms, such as autotrophic, heterotrophic, and fungal strains, has been employed. Pyrite oxidation has been described using autotrophic bacteria such as Acidithiobacillus ferrooxidans [3, 10, 15, 16]. Biodesulfurization is a biochemical reaction facilitated by aerobic microorganisms in an aqueous medium that causing in sulfur content oxidation and dissolves into sulfate [17, 18]. Biodesulphurization of high pyritic sulfur coal was studied by Pandy et al. [19]. Approximately 80% of the pyritic sulfur and 75% of the ash in the coal were removed. The removal of two Colombian coals by mesophilic bacteria was examined by Cardona et al. [18], and around 90% of the pyritic sulfur was eliminated. A newly identified Fusarium oxysporum FE has been shown to remove 34.21 % of sulfur from high-sulfur coal taken from Isfahan's Zobahan Factory [2]. In addition, some heterotrophic bacteria, including, Achromobacter [20], and Mycobacterium sp. G3 [21], and Rhodococcus erythropolis [22] can also succeed in biodesulfurization. Furthermore, some fungal strains, such as Aspergillus sp. DP06 has been employed for the biodesulfurization of Yihai coals, with a maximum total sulfur removal of 47 % [23].

Most of the pyritic sulfur in Tabas coal samples is fine-grained and cannot be removed by flotation and magnetic separations methods. Finding a method that is both suitable for the removal of coal ash and removes organic sulfur efficiently from fine-grained coal is necessary [26]. Several authors have compared and evaluated various coal

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desulfurization methods in the literature. Ahmad et al. recently compared and evaluated several different acidic and base solutions, including H_2SO_4, HCl, HNO_3, KOH, NaOH, and Na_2CO_3, for the desulfurization of the Lakrah coal [24]. Irum et al. investigated the desulfurization of Chakwal coal using three oxidants, namely KMnO4, Fe2(SO4)3, and NaOCl [25]. However, the evaluation of chemical (acidic and alkaline) and biological (bioleaching) techniques together has rarely been reported. A study was conducted in this paper to evaluate the effectiveness of chemical (acidic and alkaline) and biological (bioleaching) methods to remove pyrite sulfur, organic sulfur, and ash from fine-grained Tabas coal samples.

2. Materials and methods

2.1. Coal samples preparation and characterization

The coal samples were collected from the Parvadeh coal mine, Tabas, Iran. The samples were crushed by the laboratory jaw and cone crusher initially. Heavy media separation experiments were conducted on initial feed particle size bigger than 0.5 mm. Flotation experiments on particle size less than 0.5 mm were also carried out from (C_1), (B_2), and Eastern Parvadeh (PE) layers. The flotation concentrates and heavy media concentrates were then blended and ground with a rod mill in two sizes of 350μm and 180μm, abbreviated as B_4C_1, B_4B_4 and PE-C (PE: Eastern Parvadeh initial feed sample, PE-C: flotation and heavy media concentrate blended sample from Eastern Parvadeh layer, B_4B_2: flotation and heavy media concentrate blended sample from B_2 layer, B_4C_1: flotation and heavy media concentrate blended sample from C_1 layer). The ultimate analyses of the coal samples were prepared based on the ASTM D3176-09 standards [27]. The total sulfur, pyritic sulfur, organic sulfur, and ash content of the samples are presented in Table 1. All chemical reagents were purchased with high purity from Sigma-Aldrich.

Table 1. Analysis of sulfur and ash content of Tabas coal samples.

Samples	Code	Total sulfur (%)	Pyritic sulfur (%)	Organic sulfur (%)	Ash (%)
PE	Sample-1	1.85	1	0.85	8.11
PE-C	Sample-2	1.39	0.42	0.97	3.99
$\mathbf{B_4B_2}$	Sample-3	2.32	1.13	1.19	11.69
$\mathbf{B_4C_1}$	Sample-4	1.9	0.9	1	9.88

2.2. Chemical desulfurization Molten-Caustic Leaching (MCL) experiments

The MCL experiments were performed in an autoclave. The reactor used in these tests is made of stainless steel. To investigate the effect of caustic to coal ratio on the reduction of sulfur and ash contents, NaOH /coal ratio of 0.5 and 2 by weight was added to the reactor at 180 °C, 60 minutes, with a stirring speed of 150 rpm and 10% pulp density (w/v). In the next stage, to investigate the effect of time on sulfur and ash reduction, coal samples with sulfur content above 1% were tested with a caustic-to-coal ratio of 2 at different times (120 and 180 minutes). After the experiments, the solution was cooled to room temperature. Then the filtration was performed, and the coal samples were washed. Hydrochloric acid was used to remove the NaOH from the coal samples. Finally, the coal samples were dried at 60-70 °C for 5-6 hours [28].

2.3. Chemical desulfurization (Meyers) experiments

The chemical desulfurization experiments were performed in a 1000 ml Erlenmeyer flask. Initially, 30 g of coal samples were combined with 300 ml of a 0.8-1 M $Fe_2(SO_4)_3$ solution. All experiments were performed at a constant temperature of 90 ° C, a stirrer speed of 500 rpm, and 10% (W/V) pulp density. The coal solution was filtered and washed with 200 ml of hydrochloric acid 10% (V/V) at the end of the experiments. In addition, the coal sample was washed with 500 ml of water/acetone solution in a volume ratio of 2.3 (V/V) to wash away the residual elemental sulfur on the coal. Finally, the samples were placed in an oven at 60 ° C for 4-5 hours [25].

2.4. Biodesulfurization experiments

A mixed culture of mesophilic iron- sulfur-oxidizing microorganisms (Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, and Leptospirillum ferrooxidans in a ratio of 1: 1: 1) provided from the R&D Center of the Sarcheshmeh Copper Complex (Sarcheshmeh, Kerman Province, Iran). The mixed cultures were grown in a 9K liquid medium with 3.0 g $(NH_4)_2SO_4$, 0.5 g $MgSO_4.7H_2O$, 0.5 g K_2HPO_4, 0.1 g KCl, and 0.01 g $Ca(NO_3).2H_2O$ (per liter). H_2SO_4 was used to modify the pH to 1.8. The cultures, 120 ml medium, and 30 ml inoculum were incubated in 250 ml shake flasks at 150 rpm and 34 °C (mesophiles). During the bacterial growth (14 days), the pH was adjusted to 1.7. Finally, bacterial growth was monitored using ORP and pH measurements. It should be noted that the bacteria were not adapted to the coal sample, and after two weeks of bacterial growth, when the bacterial count reached 8×10^7 cell/Ml, the bioleaching experiments began.

Bioleaching experiments were carried out in 250 mL Erlenmeyer flasks at an initial pH of 1.7, 34 °C in a shaker incubator with a rate of 150 rpm at 10-20% inoculation percent and 5-10 % density pulp (w/v) for 20 days. The oxidation-reduction potential (ORP) and pH values were controlled during the experiment. A non-bacterial test (sterile medium) with similar conditions was performed for each sample to determine the effect of bacterial presence on sulfur and ash removal. For sterile experiments, only a 9k culture medium was used with coal samples and 3% (W/W) of Thymol. The solution was filtered and then washed with hydrochloric acid 10% (V/V) at the end of the experiments. Finally, the samples were placed in an oven at 60 ° C for 4-5 hours.

3. Results and discussion

3.1. Coal samples characterization

Scanning electron microscopy (SEM) studies are shown in Figure 1. pyrite is present in aggregate form in sample-1. The involvement of pyrite with clay minerals was observed in the sample. In some parts, pyrite is involved with calcite and dolomite. Other minerals detected in small quantities in the sample include ankerite, pyrrhotite, and galena(Figure 1-A). In the case of sample 2, pyrite is observed in the sample, which is accessible in most areas, and some parts are involved with calcite and clay minerals. Also, other minerals like calcite, ankerite, clay minerals, and feldspar were observed in the sample. In the case of sample 3, a significant amount of pyrite mineral is observed in the sample. The involvement of pyrite and calcite and pyrite and quartz are also observed in sample 3. Apatite involved with quartz was also identified in this sample.

It should be noted that a small amount of iron oxide is also present in the sample. About sample-4, a significant amount of pyrite is observed in the sample, which is free in most areas and involves clay minerals in some parts. Involvement of pyrite and calcite exists in small parts of the sample. Iron oxide minerals were also detected in the sample. Other minerals identified in the sample that are present in small quantities include barite, smithsonite, and galena.

Based on the petrography study in Figure 2, it can be observed that the Eastern Parvadeh (Sample-1) contains vitrinite and fusinite macerals. Vitrinite is the most abundant maceral in the sample and covers about 70 to 75% of the sample. Fusinite, with an abundance of about 8 to 10%, is another important maceral. Pyrite could be of organic origin and with a size of less than 0.2 mm, which is in the form of framboidal and has a frequency of about 2% in the sample. The second type of pyrite is associated with mineral origin, which has a frequency of about 1 to 2% and has been seen in the sample with a replacement texture. Vitrinite is the most abundant maceral in sample 3 and comprises about 70% of the sample. Fusinite, with an abundance of about 10%, is another important maceral of this sample. In sample 3, pyrite is about 2-3% abundant. Studies of layer sample-4 showed that vitrinite is the most abundant maceral and comprises about 75% of the sample. With an abundance of about 8%, fusinite is another important maceral. The characteristics of pyrite in this layer are the same as the primary feed of the Eastern Parvadeh (PE) sample.

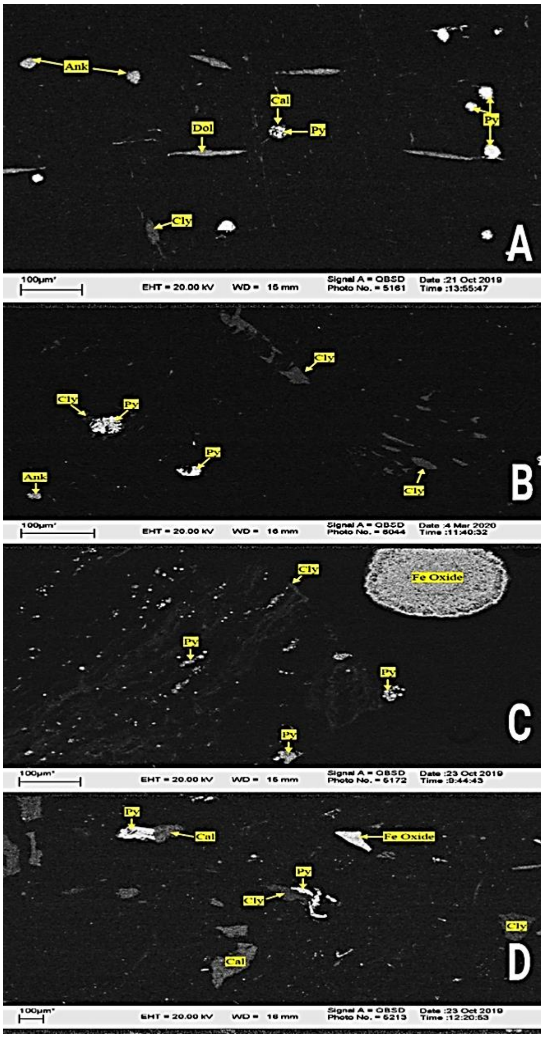

Figure 1. Scanning electron microscope (SEM) images of Tabas coal samples: A) sample-1, B) sample-2, C) sample-3, D) sample-4,
Py: Pyrite, Cal: Calcite, Fe-oxide: Iron oxide minerals, Cly: Clay Minerals, Dol: Dolomite, Ank: Ankerite.

3.2. Molten-Caustic Leaching (MCL)

Under standard conditions, Molten-Caustic Leaching (MCL) is a suitable chemical method to remove more than 90% of total sulfur and ash from coal samples [29]. Usually, more than 50% of coal ash is composed of SiO_2 and other derivatives. In this process, SiO_2 reacts with Molten-Caustic to form sodium silicate. Most of the ash components are not directly related to the organic structure of coal, and therefore, in the first stage of the reaction, ash components react with Molten-Caustic and are converted to soluble salts [30]. The MCL process can properly remove pyrite, organic sulfur, and ash from coal samples. The chemical reactions that result in the removal of inorganic compounds from coal samples are described in Equations 1 and 2.

$$2\,NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O \tag{1}$$

$$20\,NaOH + 4\,FeS_2 \rightarrow 4\,NaFeO_2 + 8\,Na_2S + 10\,H_2O + O_2 \tag{2}$$

The effect of the Caustic to coal (NaOH / Coal) ratio on sulfur and ash reduction is presented in Tables 2 and 3. As shown in Table 3, the highest reductions in total sulfur, pyrite, organic matter, and ash content are 57.84%, 88%, 24.74%, and 71.82%, respectively. It is also known that the sulfur and ash removal rate in coal samples has increased at 180 ° C and 60 minutes as the ratio of Caustic soda to coal (NaOH / Coal) enhanced from 0.5 to 2. However, it should be noted that the sulfur reduction in sample-3 and sample-4 was low, which could prove that organic sulfur is involved with the structure of coal, or pyrite particles were distributed as a fine-grained texture in the coal structure. In all coal samples with an increasing Caustic soda to coal (NaOH / Coal) ratio, the ash was appropriately removed, indicating that the ash compounds of Tabas coal are not related to the main structure of coal and are easily removed. In addition, to investigate the effect of time on reducing sulfur and ash from Tabas coal samples, the Caustic soda to coal (NaOH / Coal) ratio was considered constant at 2, and the test temperature was considered constant at 180 °C.

As shown in Table 3, increasing the time from 60 to 120 and 180 minutes reduced the organic sulfur, pyrite, and total sulfur. The highest reduction of total sulfur, organic sulfur, pyrite, and ash of product samples equals 28.45%, 23%, 38.93%, and 71.46%, respectively. In addition, the ash percentage did not change significantly with increasing time, and therefore it can be concluded that the ash does not interfere with the organic structure of coal and, in the first stages of the reaction, becomes soluble, but organic sulfur and pyrite are involved with coal macerals.

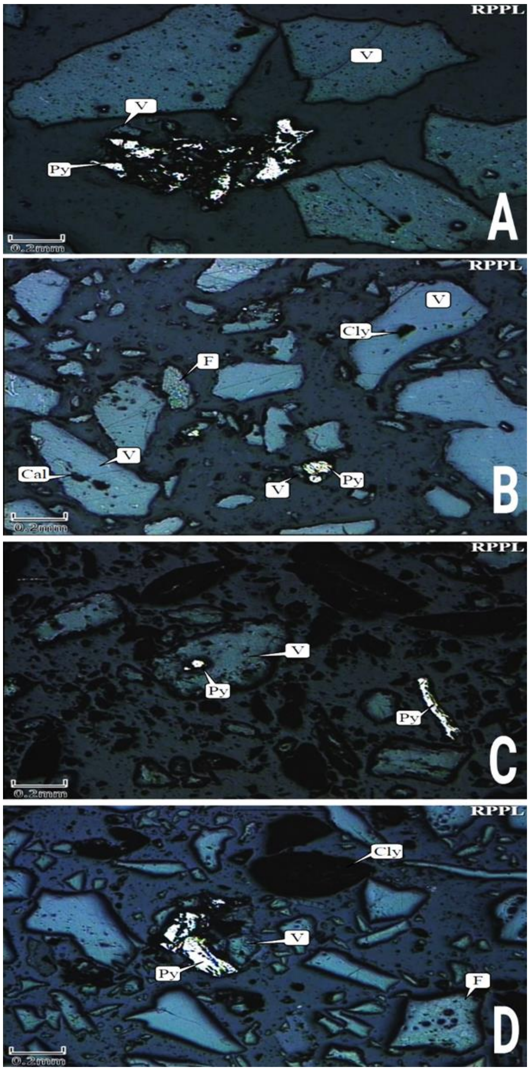

Figure 2. Polarized light microscope images of Tabas coal samples: A) sample-1, B) sample-2, C) sample-3, D) sample-4. Py: Pyrite, Cal: Calcite, Cly: Clay Minerals, F: Fusinite, V: Vitrinite.

Table 2. Effect of NaOH to Coal ratio on sulfur removal from coal samples in 60 minutes at a constant temperature of 180 ° C and a particle size of 180 microns.

Samples	NaOH/Coal ratio	Total sulfur (%)	Total sulfur removal (%)	Pyritic sulfur removal (%)	Organic sulfur removal (%)	Ash removal (%)
1	0.5	1.39	24.86	41	5.88	71.34
1	2	0.78	57.84	88	24.70	71.82
2	0.5	1.1	20.86	16.67	22.68	60.71
2	2	0.85	38.85	71.43	24.74	62.44
3	0.5	2.27	2.15	7.79	0.84	60.94
3	2	2.23	3.88	7.89	0.84	71.16
4	0.5	1.8	5.26	10	1	63.98
4	2	1.75	7.89	14.44	2	62.93

Table 3: Effect of leaching time on sulfur and coal ash removal in NaOH / Coal ratio 2, constant temperature of 180 ° C, and particle size of -180 microns.

Samples	Time(min)	Total Sulfur removal (%)	Organic Sulfur removal (%)	Pyritic Sulfur removal (%)	Ash removal (%)
4	120	20	8	33.33	63.13
4	180	28.42	23	34.44	64.74
3	120	21.12	17.65	24.78	71.31
3	180	28.45	18.49	38.93	71.46

3.3. Meyers method

Many conventional acids such as HCl, HF, and H_2SO_4 dissolve mineral salts but have an insignificant effect on pyrite sulfur. On the other hand, pyrite sulfur may be separated from coal and converted to sulfate substances using strong oxidizing agents such as H_2O_2 and HNO_3. It should be noted that ferric sulfate has been used in these experiments due to its particular property of removing pyrite. In addition, this oxidative agent has no significant effect on the organic sulfur present in coal macerals. Pyrite reacts with ferric sulfate in aqueous media at temperatures between 90-130 °C through Equations 3 and 4.

$$FeS_2 + 7Fe_2(SO_4)_3 + 8\ H_2O \rightarrow 15FeSO_4 + 8H_2SO_4 \tag{3}$$

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S \tag{4}$$

This process was initially developed by Meyer [31]. Also, the iron (II) sulfate produced by the experiment can be reduced by oxygen and is thus converted back to iron (III) sulfate, Equation 5.

$$4\ FeSO_4 + 2H_2SO_4 \rightarrow\ 3FeSO_4 + 2S \tag{5}$$

The first attempt to remove pyrite from coal was made by Yarovskii based on the oxidation of pyrite by the iron (III) sulfate in the aqueous medium to obtain elemental sulfur [32]. It has also been shown that minerals, especially alumina in ash and iron (II) sulfate, reduce desulfurization speed because of their affinity to adsorbed on pyrite surfaces. The effect of particle size on the removal of sulfur and ash from Tabas coal samples was examined in Table 4 and Table 5. The highest total sulfur, pyrite, organic sulfur, and ash removal are 51.35%, 82%, 24.74%, and 61.78%, respectively. It was observed that the finer the particle size, the higher the sulfur and ash removal rate. Smaller coal particles increase the contact surface of pyrite to react with iron (III) sulfate solution, which causes the reaction to occur more rapidly, and the iron (II) sulfate do not have enough time to precipitate on the surface of the pyrite. The Eastern Parvadeh concentration (sample-2) had fine particle size, the lowest alumina content, and the highest pyrite sulfur removal. Mokhtar et al. have reported similar results in intensely increasing pyrite sulfur removal by reducing particle size [33]. Based on Table 4, in the 180μm particle size, the total sulfur reached about 1%, except for sample-3, which is proper for the steel industry. Also, in the iron (III) sulfate solution, up to 24.74% of organic sulfur has been removed, but usually, in the Meyer experiments, only pyrite can be removed. In addition, particle size does not affect coke number, and during these experiments, coke number did not reduce. Other experiments were performed on these samples for 60 minutes at a concentration of iron (III) sulfate of 0.8 M. the experiments were performed at a temperature of 60 °C, as shown in Table 5. The reaction shown in Equation 6 shows that the acidic medium is unsuitable for the oxidation of pyrite by iron (III) sulfate [34]. Note that in an acidic medium with pH> 2, the Fe^{+3} is converted to $Fe(OH)_3$. This reaction product will precipitate as a gelatinous layer on the pyrite surface and, as a result, can prevent the desulfurization of coal samples. So the solution should first be filtered and then washed with 10% HCl (V/V); otherwise, iron (III) sulfate residues on the coal will precipitate as the pH rises, and ash analysis will be difficult. The coal sample was washed with acetone to remove sulfur remains.

$$Fe^{+3} + 3OH^{-} \rightarrow Fe\ (OH)_3 \quad ,\quad (\ pH = 2\text{-}4\ ) \tag{6}$$

3.4. Biodesulfurization

Biological oxidation is based on the ability of bacteria to oxidize sulfur compounds in coal and convert them to water-soluble compounds. Changes in acidity, total iron, and trivalent iron can be used to evaluate the desulfurization of coal during the biological process [35, 36].

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^{+} \tag{7}$$

$$Fe^{2+} + 0.25O_2 + H^{+} \rightarrow Fe^{3+} + 0.5H_2O \tag{8}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^{+} \tag{9}$$

According to Table 6, It was observed that with increasing time and also the amount of bacterial volume from 10% to 20%, the sulfur and ash removal in all three samples of Tabas coal has increased. Accordingly, the highest reduction of sulfur and ash was obtained during 20 days of bioleaching with a 20% volume of mesophilic bacteria. Organic sulfur was significantly also removed from the coal sample along with pyrite sulfur. As mentioned earlier, the biological process only leads to the oxidation of pyrite in coal macerals and does not affect organic sulfur. So, in the presence of mesophilic bacteria, organic sulfur must remain unaffected [37]. For this reason, the removal of organic sulfur up to 60% can be due to acidic media with a pH of 1.7 within 10 to 20 days of bioleaching. The best bioleaching result to remove sulfur and coal ash was carried out over 20 days with 20% bacteria. Table 7 shows the removal of sulfur and coal ash in the absence of microorganisms. Accordingly, it can be seen that the rate of sulfur and ash removal has been significantly reduced compared to the presence of microorganisms, but about 50% of pyrite sulfur and 32.43% of the total sulfur in the PE sample have been removed. It can be because of the presence of coal in acidic conditions. Based on Figure 3, for sample-1, the initial pH of the solution on the first day was set to 1.7, but in the following days, the pH decreased significantly and reached 1.4 on the 11th day and reached 1.53 on the 20th day. In addition, Figure 4 shows that on the first day, for the PE sample, the ORP was equal to 635, but on the fourth day, it decreased to 530. It continued to grow until the 20th day and finally reached 657. The initial decrease in pH in the bioleaching experiment is related to pyrite oxidation in the solution [38, 39]. Jorjani also showed that the oxidation of sulfides causes the production of sulfuric acid in solution, reducing the pH [40]. The initial pH at the beginning of the experiment was 1.7 and during the following days did not rise. The pH decreased until about the 11th day, indicating

Table 4. Effect of particle size on the removal of sulfur and coal ash at the 1M concentration of ferric sulfate, 90 minutes, constant temperature of 90 °C, and pulp density of 10% (W/V).

Samples	Particle size (μm)	Total sulfur (%)	Total sulfur removal (%)	Pyritic sulfur removal (%)	Organic sulfur removal (%)	Ash removal (%)
1	180	0.9	51.35	82	15.29	61.78
1	350	0.98	47.03	77	11.76	50.68
2	180	0.81	41.73	80.95	24.74	24.81
3	180	1.26	45.69	73.45	19.33	11.63
3	350	1.74	25	39.82	10.92	7.87
4	180	1.04	45.26	77.78	16	17
4	350	1.29	32.10	55.55	11	13.46

Table 5. Removal of sulfur and coal ash in ferric sulfate concentration 0.8M, time 60 minutes, constant temperature 90 °C, and solid percentage of 10% (W/V).

Samples	Particle size (μm)	Total sulfur (%)	Total sulfur removal (%)	Pyritic sulfur removal (%)	Organic sulfur removal (%)	Ash removal (%)
1	180	0.92	50.27	80	15.29	54.38
1	350	1.06	42.70	74	5.88	41.43
2	180	0.86	38.13	69.05	24.74	8.52

Table 6. Effect of bacterial inoculum and time on the removal of sulfur and ash from Tabas coal samples with a pulp density of 5%.

Samples	Bacterial inoculum %(v/v)	Time (day)	Total sulfur (%)	Total sulfur removal (%)	Pyritic sulfur removal (%)	Organic sulfur removal (%)	Ash removal (%)
1	10	10	0.8	56.76	79	30.59	63.12
1	10	20	0.63	67.03	90	37.64	67.09
1	20	10	0.66	64.32	84	41.18	65.18
1	20	20	0.51	72.43	92	49.41	68.98
4	10	10	0.84	55.78	61.14	51	44.46
4	10	20	0.73	61.58	67.78	56	49.31
4	20	10	0.78	58.95	64.44	54	46.71
4	20	20	0.62	67.36	74.44	61	52.12
3	10	10	1.12	51.72	77.88	26.89	31.12
3	10	20	0.91	60.77	89.38	33.61	35.71
3	20	10	0.98	57.76	84.07	32.77	32.33
3	20	20	0.81	65.09	91.15	40.34	37.12

Table 7. Removal of sulfur and ash from Tabas coal samples in the absence of microorganisms in 5% pulp density and 20 days.

Samples	Bacterial inoculum %(v/v)	Total sulfur (%)	Total sulfur removal (%)	Pyritic sulfur removal (%)	Organic sulfur removal (%)	Ash removal (%)
1	-	1.25	32.43	50	11.76	36.18
4	-	1.54	18.95	23.71	14	23.18
3	-	1.93	16.81	23.89	10.08	19.17

proper bacterial activity in the solution. In these conditions, the bacteria break the bond between sulfur and iron in the pyrite in coal, and as a result, insoluble sulfides are converted to water-soluble sulfate compounds. Also, the divalent iron released from pyrite is converted to trivalent iron by losing electrons and remains in the solution. Note that the formation of sulfated compounds, such as sulfuric acid and trivalent iron, decrees the pH. Also, the pH increased from the 11th day, indicating the end of bacterial activity and the beginning of their death phase.

In the first days, ORP was slightly decreased, possibly due to the increasing iron (II) in the solution. When bacteria break down the bond between sulfur and iron in pyrite, iron is released in the form of iron (II), which can temporarily lower ORP. Additionally, as seen in Figure 3, the ORP, or iron (III) to soluble iron (II) ratio, from the fourth-day growth suggests excellent bacterial activity in the solution. The bacterium converts iron (II) to iron (III) by accepting electrons from iron (II) separated from the pyrite bond, eventually increasing the ORP. The effect of Pulp density on the removal of sulfur and ash from Tabas coal samples in 20 days with 20% by volume of bacteria is shown in Table 8. Accordingly, in all three coal samples, at a pulp density of 10%, only about 4-5% of sulfur was reduced compared to a pulp density of 5%, but in all cases, the total sulfur was below 1%. It has been shown that this type of coal with this feature is very suitable for use in the steel industry.

3.5. Highest Sulfur/ash removal by bioleaching, Meyers, and MCL methods

As discussed in previous parts, acidic (Meyers), alkaline (MCL), and biological leaching methods have all been used in this study to achieve high coal desulfurization and ash removal from Tabas coal samples. Under the conditions mentioned above, the best results of total sulfur removal in each series of experiments can be seen in Figure 4. Accordingly, the highest sulfur removal was obtained by bioleaching experiments, in which 72.43% of the total sulfur was removed in the Eastern Parvadeh (sample-1). So, biological leaching showed the highest ability to remove total sulfur under the conditions mentioned above compared to MCL and Meyers methods. Although bioleaching with mesophilic microorganisms shows the practical ability to remove total sulfur, the only problem with this method from an economic point of view is the low kinetic compared to other methods.

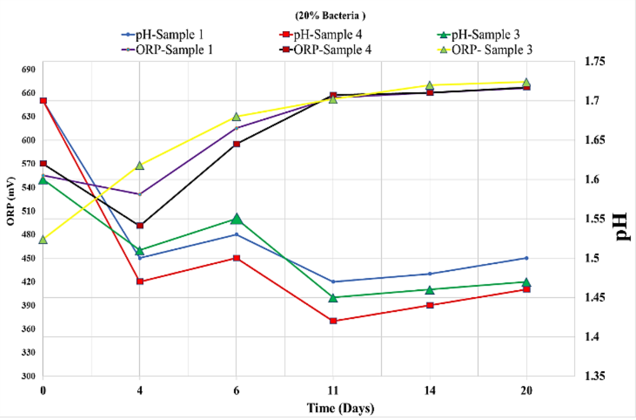

Figure 3. Evaluation of pH and ORP during 20 days of bioleaching with 20% bacterial inoculum % (v/v).

Table 8. Effect of pulp density on the removal of sulfur and ash from Tabas coal samples in 20 days with 20% bacterial inoculum.

Samples	Pulp density (%)	Total sulfur (%)	Total sulfur removal (%)	Pyritic sulfur removal (%)	Organic sulfur removal (%)	Ash removal (%)
1	5	0.51	72.43	92	49.41	68.98
1	10	0.6	67.57	89	42.35	67.56
4	5	0.62	67.36	74.44	61	52.12
4	10	0.71	62.63	65.55	60	50.11
3	5	0.81	65.09	91.15	40.34	37.12
3	10	0.89	61.64	87.61	36.97	35.91

On the other hand, the cost of chemicals and energy in biological methods is negligible compared to chemical methods. Figure 5 shows the best results of ash removal from the performed methods. Accordingly, the highest ash reduction was related to the sample of Eastern Parvadeh feed with 71.82%, which was obtained in MCL experiments. The best ash removal results after MCL tests are related to biological and Meyers methods, respectively. The main reason for the high removal of ash in the MCL method compared to other methods can be the high temperature and pressure during the test and the ability of the molten soda to react with the ash content of the Tabas coal. Chemical coal desulfurization is not economical at the moment; it may become economical in the future [41]. Desulfurization methods are often regarded as the most efficient approaches for inorganic and organic sulfur removal, but they are complex, costly, and need high temperatures [11]. Biological desulfurization is more environmentally friendly than other approaches. It has easy installation and low energy consumption and is incredibly attractive for removing pyritic sulfur from coal [42]. Therefore, based on environmental concerns and investment costs, it seems that the biological method would be more appropriate to remove sulfur from Tabas coal among all three methods applied in the present study.

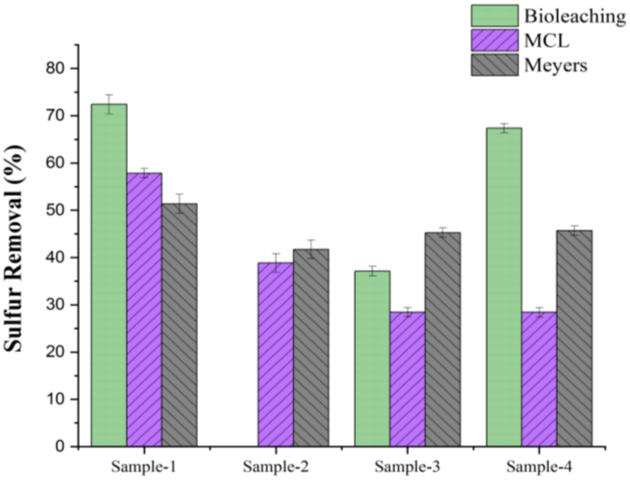

Figure 4. Sulfur removal from Tabas coal samples using bioleaching, Meyers, and MCL methods.

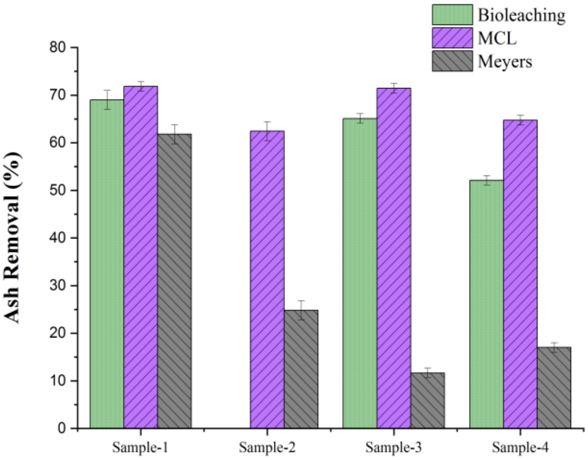

Figure 5. Ash removal from Tabas coal samples using bioleaching, Meyers, and MCL methods.

4. Conclusions

Tabas coal samples have a high coke number, so if their sulfur and ash reach below 1% and 10%, respectively, they can be used in the steel industry. In this study, acidic (Meyers), alkaline (MCL), and biological leaching methods were used to reduce the sulfur and ash content of Tabas coal samples. Accordingly, in acid leaching, at 90 °C, 90 minutes, pulp density of 10% and concentration of 1 M iron (III) sulfate, 51.35% of total sulfur, and 61.78% of ash were removed from the Eastern Parvadeh sample. Furthermore, particle size had the most significant effect on desulfurization in these experiments. Also, in alkaline leaching (MCL) NaOH / Coal ratio of 2, the temperature of 180 ° C, and 60 minutes, 57.84% of the total sulfur and 71.82% of the ash were removed from the Eastern Parvadeh sample. Also, the most significant effect of pyrite and organic sulfur removal was related to the time of the experiment. Finally, in biological experiments, at a temperature of 34 ° C, 20 days and 5% pulp density, 72.43% sulfur and 68.98% ash from the Eastern Parvadeh samples were removed. In these experiments, the time has the most significant effect on total sulfur removal. Based on environmental concerns and investment costs, it seems that the biological method would be more appropriate to remove sulfur from Tabas coal among all three methods applied in the present study.

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