Article

Bioleaching Coal Gangue with a Mixed Culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*

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Abstract: A mixed culture of *A. ferrooxidans* and *A. thiooxidans* isolated from a coal gangue dump was used to bioleach coal gangue in a column reactor to investigate the leaching of elements. The changes of metal ions (Fe, Mn and Cr) and sulfate in the leaching solution, elemental composition, mineral components and sulfur speciation of the coal gangue before and after bioleaching were analyzed by atomic absorption, anion chromatography, XRF, XRD and XPS. The results show that the mixed culture could promote the release of metal ions in coal gangue, with a leaching concentration of Fe > Mn > Cr. EC and Eh have significantly increased with the increase of metal ion concentrations in the leaching solution. XRF analyses show that the contents of Fe, Mn and S decreased in coal gangue after bioleaching. XRD results suggest that the bioleaching has impacts on minerals in coal gangue, particularly the Fe-containing components. XPS analyses show that sulfur speciation in the raw gangue samples was associated with sulfate, dibenzothiophene and pyrite sulfur. After continuous leaching by the mixed culture, the total sulfur, pyrite sulfur and sulfate sulfur in coal gangue decreased from 2.06% to 1.18%, 0.66% to 0.14% and 1.02% to 0.52%. The desulfurization rates of the pyrite and sulfate were 78.79% and 49.02 %. It is concluded that the mixed culture of these two microorganisms could effectively leach metals from coal gangue coupling with the oxidation of sulfide to sulfate. This study has provided fundamental information as a potential application in the recovery of valuable metals from coal gangue or environmental remediation related to gangue in the future.

Keywords: bioleaching; coal gangue; mixed culture; metals; sulfur speciation

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1. Introduction

Coal mining and processing have generated massive coal gangue and accumulated as gangue dumps. The leaching, weathering and biological catalysis of coal gangue can release metals and sulfur into the environment. Furthermore, the formation of acid mine drainage (AMD) from oxidation of pyrites and other sulfur-bearing minerals in coal gangue causes serious environmental pollution to the air, surface water and surrounding soil [1,2]. There has been concerns over the pollution caused by coal gangue dumps. As such, the number of reports related to environmental pollution and risk assessment of sulfur and metals has increased in the past thirty years [3,4]. However, coal gangue also contains

valuable elements and minerals, which can be used as a potential resource for recovery. Guo [5] had successfully produced $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ from an acid leaching liquor of coal gangue by using concentrated hydrochloric acid. Xiao [6] reported recovery of Al and Si from coal gangue by acid leaching with an elevated temperature. Zhang and Honaker [7] recovered rare earth elements and other critical metals (Co, Cr, Li, Mn, Sr, and V) from calcination products of coal gangue by acid leaching and sequential chemical extraction. However, the study of metal leaching from coal gangue by microorganisms is limited [8].

It is well established that numerous microorganisms can inhabit around coal gangue dumps [9], among which sulfur-oxidizing bacteria (SOB) and ferrous oxidizing bacteria (FOB) are the most common ones. These bacteria have been used to remove sulfur and metals from coal gangue or coal because of their capability of increasing sulfur mobility by oxidation and dissolution of metal species [10]. Aytar [11] reported that the inorganic sulfur of coal was successfully removed by bioleaching of *A. ferrivorans*. Mishra [12] used a two-step sequential leaching method with *Sinomonas flava* 1C and *A. ferrooxidans*. It was found that the desulphurization was enhanced with a sulfur removal rate of 50 to 53%. Studies also show that bio-desulfurization could be related to nutrients [13]. Chen [8] used *A. ferrooxidans* for the bioleaching of coal gangue and found that the liberation of iron, manganese and chromium increased. Sarswat [14] recovered rare earth elements from coal-based resources with a bioleaching approach. Furthermore, studies have shown that the mixed cultures of bacteria could effectively improve the bioleaching rate of valuable metals from metal sulfide [15–17]. In addition, studies also showed that a mixed culture of SOB and FOB can seemingly improve the removal of sulfur [18]. Oxidation and speciation of sulfur are the main biochemical processes in metal sulfide bioleaching. Liang [19] reported that the addition of sodium chloride could effectively reduce the accumulation of elemental sulfur during bioleaching of chalcopyrite by a thermophile *Acidianus manzaensis*. In one study, S^0 deposited on the mineral surface was eliminated by the sulfur oxidation of *A. ferrooxidans* assisted by polyethylene glycol [20]. In another, Fe^{3+} and *Sulfobacillus thermosulfidooxidans* synergistically promoted S^0 and As_2S_3 removal during arsenopyrite bioleaching [21].

SOB and FOB have been found to accelerate metal leaching, sulfur oxidation rates of metal sulfide and bio-desulfurization of coal or coal gangue. All these suggest that the mixed cultures of bacteria could improve sulfur removal from coal gangue. However, the information about bioleaching of metal ions with mixed bacteria and sulfur oxidation in coal gangue remains unknown. In the present work, two microbial strains *A. ferrooxidans* SOB-1 (AF) and *A. thiooxidans* SOB-2 (AT), isolated previously, were employed in continuous leaching experiments of coal gangue. Metal ions and sulfate concentrations in the leaching process, the elemental concentrations, and the minerals and sulfur speciation before and after bioleaching were analyzed by atomic absorption, anion chromatography, XRF, XRD and XPS. The overall aim of the present study was to obtain information on the possibility of using coal gangue as a source for metal extraction with bacteria and investigation of bioleaching mechanisms. This could have an important ramification of extracting valuable metals from coal gangue using microbes.

2. Materials and Methods

2.1. Microbes and Coal Gangue Sample

A. ferrooxidans SOB-1(AF) (Accession number in Genbank: KR856280) and *A. thiooxidans* SOB-2 (AT) (Accession number in Genbank: KR856281) used in bioleaching experiments were isolated previously in our laboratory [22]. AF and AT were inoculated in 250-mL flasks containing 100-mL 9K medium and incubated at 30 °C and 170 rpm [13]. The initial density of the cells was 1.0×10^7 cells/mL. Bacterial cells were collected at the late exponential phase. The culture solution was filtered three times through a filter paper with pore sizes of 7–10 μm to remove any suspended solids. The filtrate was centrifuged at 10,000 rpm for 15 min. The pellet containing cells was washed thrice with diluted sulfuric acid (0.1 mol/L) to remove trapped ions.

The coal gangue sample was obtained from a coal gangue dump in Liejiaqiao coal mine (43°69'65'' N, 112°43'47.66'' E) in Xiangtan, Hunan Province, China. The fresh coal gangue was crushed and sieved to various particle sizes for further usage.

2.2. Bioleaching Experiment of Coal Gangue

A column-type flow-through reactor was designed and fabricated to study the bioleaching of coal gangue [23]. As shown in Figure 1, the continuous leaching system was composed of a leaching column, a pump (DHL-A, Shanghai HuXi Analysis Instrument Factory Co., LTD, Shanghai, China), an electric stirring apparatus and a water bath. The leaching column was made from a PVC pipe with a dimension of 50 cm (length) and 9 cm (inner diameter). A supporting plate was fixed at the bottom of the column with a round hole of size 0.3~0.4 mm for draining. The column was packed with the coal gangue. The culture solution (10% mixed bacteria in 9K medium) or the sterile 9K medium (as the control) was pumped continuously to the top of the column. The leachate was drained by gravity. A 2-L beaker was placed in a water bath at 30 °C for collecting the leaching solution. Both the column and beaker were covered to minimize contamination and water evaporation. Previously, it was determined that it was beneficial to use a mixed culture for sulfur oxidation [17]. In this work, the mixed culture was prepared at a ratio of 1:1 with AF and AT. For practical purposes, the column was packed with two layers of coal gangue with different particle sizes, i.e., the bottom layer with 0.3 kg had particle sizes between 8–10 mm and the top layer with 1 kg had particle sizes of 1–4 mm. A volume of 1700 mL culture solution or medium solution was run through the column at a fixed flow rate of 10 mL/min for 74 days. Sterile deionized water was added on a regular basis to make up the evaporation. The pH, electronic conductivity (EC) and redox potential (Eh) were measured with a pH meter (PHS-3C, Leici, Shanghai, China), a conductivity meter (DDS-11A, Leici, Shanghai, China) and an ORP electrode (501, Lei-ci, Shanghai, China). An aliquot of 5 mL leaching solution was collected at an interval of four days to determine pH, Eh and EC. Concentrations of Fe, Mn and Cr were determined by atomic absorption spectrometry (TAS-986, General Analysis, Beijing, China) [24]. The concentration of SO_4^{2-} was measured with ion chromatography (ICS-1500, Dionex, Sunnyvale, CA, USA). The correlation analysis among pH, Eh, EC, Fe, Mn, Cr and sulfate were analyzed with SPSS Statistics 17.0 for Windows (SPSS Inc, Chicago, IL, USA). All the tests were run in triplicate. Mean values of the triplicate of the leaching experiments were presented.

2.3. Sample Analyses

By the end of the bioleaching, 50 g of coal gangue were collected from the column. The samples were washed 3 times with deionized water, vacuum freeze-dried for 10 h and ground to a particle size of 0.074 mm for further analyses. The total sulfur of raw, test and control gangue samples was analyzed according to the methods of China National Standards (GB/T 214-2007). The elemental contents, mineral components and sulfur speciation were investigated by XRF, XRD and XPS.

XRF: Elements of raw, test and control coal gangue samples were analyzed by XRF (Bruker Tiger S₈, Karlsruhe, Germany) using a rhodium target and 75 µm Beryllium-window with a high voltage power supply up to 4 kw, 60 kV and 170 mA. It equips with three crystal changers (PET, XS-55 and LiF200) for different element analyses.

XRD: Main mineral components of raw, test and control coal gangue samples were analyzed by XRD (Bruker D8, Karlsruhe, Germany) with Cu K α radiation generated at 30 mA and 40 kV, operated at 0.02 two-theta steps from 3° to 80° and a count time of 0.02 s per step.

Figure 1. Column-type flow-through reactor.

XPS: Sulfur speciation analysis was conducted with XPS (Thermo Fisher ESCALAB250Xi, Waltham, MA, USA) equipped with an Al K α (1486.6 eV) source. The spectrometer was run with an analyzer pass energy of 20 eV and 100 eV for narrow scanning and wide scanning, corresponding to step energy of 0.05 eV and 1 eV. The Shirley background was subtracted. The calibration for binding energy was carried out to the main C 1s peak at 284.80 eV. The peak curves were resolved using Gaussian line shape with XPS peak 4.1 software. Concentrations of sulfur in various chemical speciation were calculated using the intensity of an appropriate line and XPS cross-sections. The relative contents of sulfur were calculated with total sulfur and relative peak areas.

3. Results and Discussion

3.1. pH, Eh and EC Variation of Leaching Solutions

The variations of pH, Eh and EC of the leaching solutions are presented in Figure 2. As shown in Figure 2a, the pH values of the leaching solutions increased initially for both the control and test groups. They peaked at 3.22 and 2.77 on the 16th d and 12th d and then continuously declined to 2.35 and 2.0 by the end of the leaching experiment. The initial pH increase can be associated with the release of exchangeable alkali ions and soluble oxides in coal gangue [25]. In coal gangue leaching, dissolution and oxidation of acid-producing minerals (such as pyrite) is likely to result in the decline of pH [26]. The decrease of pH in the test group may also be related to the oxidization of sulfur compounds (such as pyrite), forming sulfuric acid by microbes [27]. A recent study showed that low pH environments could contribute to the release and migration of metal ions as well as dissolution rates [28]. In the control, the decrease of the pH is attributed to the equilibrium between coal and the medium (acidic pH at around 2.5).

Figure 2. pH (a), Eh (b) and EC (c) of test and control groups in leaching solutions.

Eh variations of the leaching solutions are showed in Figure 2b. In general, the Eh increased over leaching time and reached a plateau with a maximum value of around 660 mV. The difference between the control group and the test group was insignificant. The test group exhibits slightly higher Eh than the control group. It is presumed that the concentration of substrates in coal gangue directly used by microbes was low and the chemical oxidation reaction had taken place in each group.

EC represents the total ionic concentration of the leaching solution. The EC variation of the leaching solutions is somehow correlated to pH values and presented in Figure 2c. Initially, the values for both control and test groups remained stable. After that (22 d), the values increased possibly because of the dissolution of the metal ions loosely bind to coal organics. In general, a lower pH has higher EC, indicating that the metal and non-metal species can dissolve easily in mine water at very low pH. After 50 d, the increases were not obvious, possibly attributed to the fact that the metal ions were not available for leaching.

High acidity and EC in AMD water discharged from active, abandoned and reclaimed coal mine sites continues to be a global concern due to variable impacts on the quality of surface water and groundwater [29]. Dutta [30] studied the cytotoxicity of AMD in an Indian high-sulfur coal mining area and found mine water samples have high conductivity and high concentrations of trace elements which are detrimental to HepG2, A549, MIAPaCa2 and L6 cell lines. Although the cytotoxic effects to the environment were not investigated in this work, it is generally accepted that the discharge of water with extremely low pH (2.0) could impair soil quality and crop productivity.

3.2. Metal Ions Concentrations

As shown in Table 1, the main elements in raw coal gangue include Al, Fe, Ti, Mg, Cr and Mn. These elements can be recycled and yet reduce the impacts on the environment. As shown in Figure 3, in general, the ion concentrations of Fe, Cr and Mn increased with the leaching time. During 74 days of treatment, Fe concentration increased from 16.1 to 195.3 mg/L, Cr from 2.2 to 137.1 mg/L and Mn from 9.6 to 92.7 mg/L. In general, the release of metal ions is positively correlated to their concentrations in coal gangue which agrees with previous studies [2,31,32]. For the extraction of Fe, the leaching can be divided into four stages. Initially (1–18 d), the total Fe concentration in the leaching solution remained stable, then slowly increased in the second stage (18–42 d), rapidly increased in the third stage (42–54 d) and finally entered the stationary phase (54–74 d) (Figure 3a). In the control group, the same trend was observed except that the Fe concentration was lower, suggesting the oxidation of sulfur and iron speciation have an impact on the leaching of Fe [33,34]. In a natural environment, a coal gangue dump often experiences spontaneous combustion with pyrite oxidation via air and moisture as the main chemical reaction [35]. It is speculated that the leaching behavior of iron is related to the alternate speciation caused by air oxidation and microbial reduction. On the contrary, the leaching of Cr and Mn is more pH-dependent as shown in Figure 3b,c.

Table 1. Element analysis of raw and residual coal gangue by XRF.

Element (%)	MgO	TiO ₂	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃
Raw	0.23	0.27	5.81	37.80	0.45	2.13
Control	0.20	0.30	5.37	36.90	0.31	2.01
Test	0.18	0.27	5.29	36.30	0.15	1.56
Element (mg/kg)	S	Cr	Mn	Cl	Pb	Sr
Raw	2.05	74.95	131.62	0.026	0.001	0.045
Control	1.92	48.60	102.30	0.060	0.003	0.046
Test	1.66	12.30	53.24	0.075	-	0.010

- No detected.

Figure 3. Fe (a), Cr (b) and Mn (c) concentrations in leaching solutions of test control groups.

The correlation of pH and ion concentrations was summarized in Table 2. The pH peaked at around day 16 and returned to initial pH at around day 30, at which point the release rates of metal ions started to increase for Cr and Mn (Figures 2a and 3b,c). According to our previous work, the fraction of Fe and Cr in raw coal gangue was mainly residual fraction (residual fraction is the main form of occurrence of metal elements in coal gangue, its main mineral component is clay and its chemical composition is aluminosilicate), while the majority of Mn existed as iron manganese oxide bound fraction [8]. Different leaching behavior of Fe, Mn and Cr was observed, suggesting the leaching mechanisms of the three metals are not the same. This may be related to the forms they are present in coal gangue [36,37].

Table 2. Correlation of pH, Eh, EC, Fe, Mn, Cr and sulfate.

	Time	pH	Eh	EC	Fe	Cr	Mn	SO ₄ ^{2−}
Time	1	−0.936 **	0.910 **	0.865 **	0.871 **	0.969 **	0.947 **	0.960 **
pH	−0.936 **	1	−0.795 **	−0.881 **	−0.889 **	−0.952 **	−0.957 **	−0.949 **
Eh	0.910 **	−0.795 **	1	0.781 **	0.701 **	0.849 **	0.780 **	0.796 **
EC	0.865 **	−0.881 **	0.781 **	1	0.794 **	0.938 **	0.883 **	0.825 **
Fe	0.871 **	−0.889 **	0.701 **	0.794 **	1	0.891 **	0.951 **	0.947 **
Cr	0.969 **	−0.952 **	0.849 **	0.938 **	0.891 **	1	0.975 **	0.954 **
Mn	0.947 **	−0.957 **	0.780 **	0.883 **	0.951 **	0.975 **	1	0.986 **
SO ₄ ^{2−}	0.960 **	−0.949 **	0.796 **	0.825 **	0.947 **	0.954 **	0.986 **	1

Pearson correlation, correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed).

It is generally accepted that the metals in coal gangue could be released and pose a threat to the environment. In a study, the metals in coal gangue and their ecological risk were evaluated in Suncun coal mine. It was found that Cr and Pb have a strong effect on the ecological integrity of the environment [1]. In our previous work, soil properties, microbial flora and metal profiling surrounding the coal gangue dump were investigated. The study shows that the metals from the coal gangue dump did affect the surrounding

environment [38]. Bioleaching and the recovery of metals with microbes offer an alternative way to tender this solid waste.

3.3. Sulfate Concentration

As shown in Figure 4, the SO_4^{2-} concentration of the test group increased over time and is much higher than that of the control group. The SO_4^{2-} concentration continued to increase over the entire period of the experimentation with a maximum concentration of 14.5 g/L. According to the results in Table 2, it shows that the dissolution of SO_4^{2-} has a general significant correlation with the acidity of the leaching solution, and a highly significant correlation with Eh, EC and the concentrations of three metals. This suggests that the dissolution of SO_4^{2-} is not exclusively dependent on the acidity of the culture solution. Bioleaching of pyrite follows the thiosulfate pathway. That is, the chemical bonds between sulfur and metal moieties are broken by iron (III) attack and liberate thiosulfate. Then, the free thiosulfate is oxidized to tetrathionate and other polythionates and finally to sulfate, while protons are also produced [32]. Because AF can oxidize both ferrous and reduced sulfur compounds while AT can utilize reduced sulfur compounds, the mixed culture plays an important role in promoting sulfide oxidation and hence sulfate leaching [39].

Figure 4. SO_4^{2-} concentration in leaching solutions of test and control groups.

The high sulfate concentration in soil and water has become a prominent problem as it causes corrosion [40]. One study shows that the main damage of concrete lining was caused by sulfate in groundwater for 45 years [41]. It is obvious that high concentrations of sulfate can be generated by the mixed culture in the present work. The risk of damage to the facility of coal mines should be considered.

3.4. Elemental Analysis of Coal Gangue before and after Leaching

The main elements of the residual coal gangue after leaching are shown in Table 1. The concentrations of the test group for all the elements except for Cl were lower than the control group and raw coal gangue. The changes of elements Fe, Mn, Cr, Ca, Sr and S were more substantial than other elements, e.g., Al, Si, Ti and Mg. The concentrations of Fe, Mn and Cr of the test group were obviously lower than that of the control group. This agrees with the analyses in the leaching solutions in that the concentrations of Mn, Cr and SO_4^{2-} increased with the leaching time (Figures 3 and 4). The results suggest that sulfide sulfur in the coal gangue was oxidized by the microorganisms, forming mainly SO_4^{2-} . In addition, the bioleaching has significantly improved the release of metal ions from coal gangue. The significant correlation between metal ions and sulfate illustrates that the leaching is mainly related to sulfide oxidation.

3.5. Mineral Components Analysis before and after Leaching

Figure 5 shows the mineral components of raw and residual coal gangue after leaching. Quartz, kaolinite and pyrite were detected in all three samples. According to the XRF analysis in Table 1, Fe, Si and Al are the main elements in coal gangue, which are also the main elements of these minerals. In the raw gangue, iron-containing minerals including pyrite, hematite and siderite, and other peaks representing calcite and titanite schorl were detected (Figure 5a). However, after leaching, the diffraction peaks of hematite, siderite, calcite and titanite schorl in the test group (Figure 5b) and control group (Figure 5c) were not detectable. Hematite and siderite are more readily soluble in acidic conditions, whereas the solubilization of pyrite involves oxidation. It is assumed that Ca and Ti in the minerals were solubilized although they were not analyzed. With CaCO_3 as its main component, calcite can be dissolved in acid solutions, while acid leaching is also a conventional technique for the recovery of titanium from ores [42]. However, the total concentration of Ti remained unchanged after bioleaching (Table 1), suggesting that there may be other major forms of Ti-containing constituents that are not accessible to bioleaching. On the other hand, several novel crystal diffraction peaks were detected in the test and control samples, indicating that the leaching process may provide a chemical environment not only for ore dissolution but also for the production of derivatives or new crystal structures.

Figure 5. Mineral composition of raw coal gangue (a), test group (b) and control group (c).

3.6. Desulfurization and Sulfur Speciation Analysis

The total sulfur in coal gangue samples were 2.06% (raw gangue), 1.06% (control) and 1.18% (test group), suggesting the mixed culture has enhanced the sulfur removal. XPS as a non-destructive method has been widely used in qualitative analysis, semi-quantitative analysis and quantitative analysis of sulfur in coal [43]. The peak fitting of the XPS analysis of the coal gangue samples is shown in Figure 6 and Table 3. The binding energy of different sulfur species is assigned to pyrite and mercaptan (162.1–163.6 eV), thiophene (164.0–164.4 eV), sulfoxides (165.0–166.0 eV), sulfone (167.0–168.3 eV) and sulfate (>168.4 eV) [44,45]. As shown in Figure 6a, the raw gangue had peaks at the binding energy of 164.2 eV, 165.3 eV and 169 eV, corresponding to pyrite, dibenzothiophene (DBT) and sulfate. As shown in Table 3, sulfate accounts for about half of the peak area of sulfur with a relative content of 1.02%. The relative content of pyrite and DBT are 0.66% and 0.38%. Pyrite content in the test group decreased from 0.66% to 0.14% with a desulfurization rate of 78.79%, whereas it remained unchanged in the control group, suggesting the dissolution of pyrite was attributed to bacteria oxidation. SOB and FOB have a special enzyme system that could enhance the oxidation of pyrite [46,47]. Under the action of microbial oxidation, sulfur is converted into sulfates and hence improved the desulfurization of gangue [48]. On the contrary, for sulfate, the control group (from 1.02% to 0.38%, or 62.75%) had a higher dissolution rate than that of the test group (from 1.02% to 0.52%, or 49.02%). This suggests that the sulfur speciation induced by the biological processes is complicated and needs further analysis. It can be speculated that the increase of sulfate concentration in the leaching solution of the test group is mainly attributed to the oxidation of pyrite by

the microorganisms. Sulfate originated from pyrite oxidation could be retained in the coal gangue matrix and explains the higher leaching rate of sulfate in the control group. Relative content of DBT in the coal gangue increased from 0.38 % (raw) to 0.52 % (test). It is speculated the organic moieties such as sulfhydryl and glutathione groups may be produced by SOB that contains similar functional groups in DBT.

Figure 6. XPS peak fitting of raw coal gangue (a), test group (b) and control group (c).

Table 3. Sulfur speciation in raw, test and control gangue samples.

Sulfur Speciation	Raw		Test		Control	
	Peak Areas %	Relative Contents %	Peak Areas %	Relative Contents %	Peak Areas %	Relative Contents %
Pyrite	31.88	0.66	11.75	0.14	45.95	0.63
DBT	18.62	0.38	44.25	0.52	12.90	0.05
Sulfate	49.49	1.02	43.99	0.52	41.14	0.38

4. Conclusions

Continuous bioleaching of metals in coal gangue was studied in a column reactor with a mixed culture of *A. ferrooxidans* SOB-1 and *A. thiooxidans* SOB-2. The present results demonstrate that the extraction of metal ions including Fe, Mn and Cr can be significantly enhanced by bioleaching processes. The leaching of metal ions has a strong relationship with pH and sulfate in the leaching solution. The release of Fe was mainly caused by the oxidation of pyrite. The main minerals in the coal gangue are pyrite, quartz and kaolinite. The leaching of Fe is attributed to the oxidation of iron sulfide by the microorganisms, while Mn and Cr are more dependent on the acidic conditions. The mixed culture has obviously improved sulfur removal from coal gangue with a reduction of total sulfur from 2.06% to 1.18%. Pyrite sulfur in coal gangue decreased from 0.66% to 0.14% (78.79%) which is also mainly attributed to bacterial oxidation. The present work implies that the valuable metals in coal gangue can be extracted with SOB and FOB. This also provides a potential application technique to the recovery of valuable metals from coal gangue or environmental remediation related to gangue in the future.

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