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Sulfur Removal from Coal with The Basic Extraction Liquid of Oak Ash

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ABSTRACT: Desulfurized coal produces high amounts of SO_X during combustion. Therefore, many negative environmental impacts such as air pollution and acid rain occur. Coal desulfurization research is very important for environmental and socio-economic development. In this study; it was aimed to desulfurization of coal with oak ash extraction liquid. In this way, sulfur compounds that are harmful to the environment were removed with a waste in nature. Sorgun coal was chosen due to its high sulfur content. Extraction liquids were obtained from different weights of oak ash. Total sulfur and pyritic sulfur values were measured after desulfurization process. In addition, KOH + oak ash liquid mixtures were used for desulfurization to determine the effect of chemicals. For Sorgun coal, the highest total sulfur and pyritic sulfur removal with oak ash were obtained as 28.7% and 57.7%, respectively. Furthermore, the highest pyritic sulfur removal with oak ash + KOH mixtures was obtained as 61.9%. As a result of the study, it was observed that the oak ash extraction liquid was effective to remove total sulfur and pyritic sulfur from coal. It is clear that this study will light on further studies for desulfurization.

Keywords: Coal, Desulfurization, Oak ash, Sulfur

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INTRODUCTION

Energy is a vital need that is necessary for human life. Throughout human history, the usage of energy has been changed owing to major reforms in human civilization. By using and developing energy, both the world economy and human society have major improvement (Feng et al., 2020a). The rapid development of the industry and the economy also increase global energy consumption. In order to supply the rapidly increasing global energy consumption, sustainable growth in the field of energy is becoming necessary (Feng et al., 2020b).

Coal, which is a nonrenewable fossil resource, has been used as the main energy source for centuries (Çelik et al., 2019). The organic and inorganic structure of coal consists of minerals such as carbon, sulfur, clay, calcite and quartz (Boylu and Karaağaçoğlu, 2018). The sulfur in coal occurs in organic and inorganic forms (Liu et al., 2020). Inorganic forms of sulfur in coal are generally found as pyrite, sulfur and sulfate (Li and Tang, 2014).

SO_X emissions from burning coal cause serious environmental problems (Ye et al., 2018). SO_2 gases generated by the combustion of coal can be oxidized in the troposphere layer of the atmosphere and converted into sulfate. At the same time, SO_2 gas, which turns into solid pollutants, is the main source of PM2.5. All over the world, millions of tons of SO_2 gas are emitted into the air during the burning of coal, especially in power plants. It can be said that this is the most important reason for the increase in acid rain (Yong-liang et al., 2020). As a result, the desulfurization process is very important to ensure clean conversion of high sulfur coals and reduce environmental effects. Various pre-desulfurization processes are applied for the desulfurization of coal. In this way, the sulfur forms in the coal are changed (Wang et al., 2020). Primary desulfurization methods can be expressed as physical, physico-chemical, chemical and bio-desulfurization. Among these methods, it can be stated that the chemical desulfurization method is the most effective method for both inorganic and organic desulfurization (Xia and Xie, 2017). The above-mentioned coal desulfurization methods are shown in Figure 1.

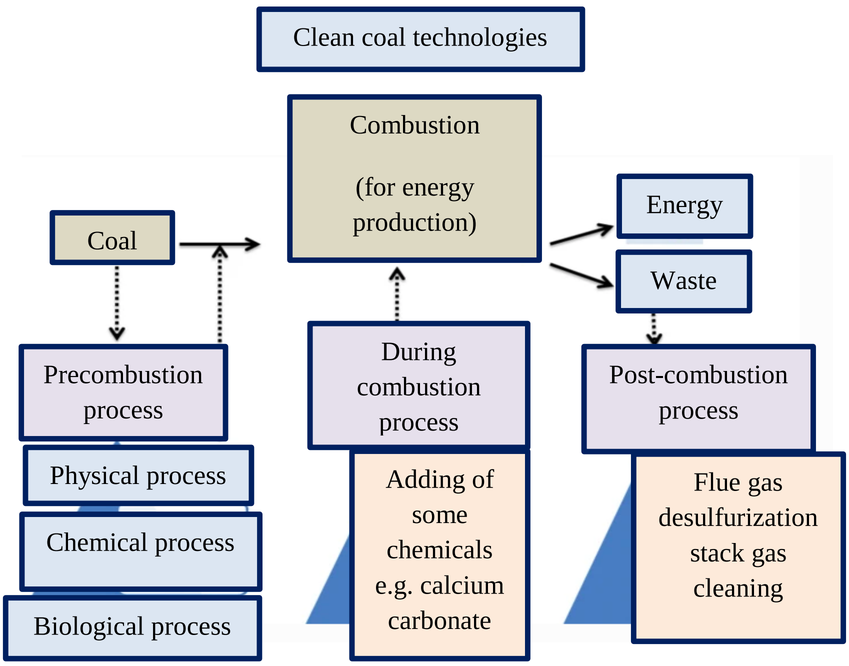

Figure 1. Clean coal technologies (Çelik et al., 2019)

Sulfur in coal can be removed by physical, chemical and biological methods. Among these methods, physical method is cost-effective and can remove pyritic sulfur but this method can't reduce organic sulfur. Both organic and inorganic sulfur from coal can be removed by chemical method (Ye et al., 2018). Many different methods applied for the desulfurization of coal are available in the literature (Tang et al., 2020).

Researches show that magnetic (Meshrogli et al., 2015), chemical (Longjun and Caixi, 2007) and biological (Kumar et al., 2019) methods are used to desulfurization of coal. Ning and Xiuxiang (2015) used a microwave method to desulfurize coal in a NaOH solution. They used K-edge X-ray absorption near-edge structures to analyze the changes in the form of sulfur before and after desulfurization and found that the pyritic sulfur content of the coal decreased from 53.6% to 39.2%. Liu et al. (2017) observed desulfurization of Yihai coalfield contains 4.97% total sulfur content. After desulfurization process with a newly isolated native bacterium Aspergillus sp. DP06, total sulfur content was reduced to 2.63%. Singh et al. (2018) investigated high-sulfur coal samples collected from Giral lignite mine were desulfurized using bacteria Burkholderia sp. GR 8–02 isolated from native lignite. After desulfurization, the total sulfur content of coal sample decreased from 4.23% to 2.99%.

Desulfurization of coal with waste material in nature instead of the physical, chemical and biological methods is an environmentally friendly desulfurization process. This method has many advantages over physical, chemical and biological methods such as less costly, reusing waste, not creating any waste material at the end of the process. Moreover; there is no published research examining the use of waste for desulfurization. The main purpose of this study is to use a waste material in nature for desulfurization process without adding chemicals or using microorganisms in desulfurization process and to determine the efficiency of this process. In this paper, the desulfurization process of Sorgun coal was examined using basic extraction liquids of oak ash. Before and after this process; the total sulfur and pyritic sulfur content of this sample were determined and removal was calculated.

MATERIALS AND METHODS

The samples were crushed to a particle size of 250 μm using the ASTM D2013 method. Total sulfur contents were measured using the IR ASTM D4239 method. Afterwards, 2 g, 4 g, 6 g, 8 g and 10 g oak ash samples were extracted in 20 mL, 40 mL, 60 mL, 80 mL and 100 mL of distilled water at 100°C for 30 min and then the mixtures were filtered to obtain basic liquid. The samples were re-extracted in the basic liquid at 100°C for 1 hour and then filtered. They were dried in an oven at 103°C for 1 hour and then leached in 100 mL HCl to remove the non-pyritic iron. They were boiled in 50 mL nitric acid solution (one volume of HNO_3 + seven volumes of pure water) in an Erlenmeyer flask with a reflux condenser for 30 min.

The mixtures were filtered after boiling. 2 mL H_2O_2 was added to filtrate and boiled to remove the discoloration due to coal breakdown and to oxidize the iron. Fe^{+3} ions in the filtrate solution were precipitated using ammonia. The filtrate solution was filtered again and then washed with hot distilled water and HCl. Its pH was adjusted to 2.5 and added 1 mL of 5-sulfosalicylic acid indicator solution.

Adjusted disodium salt of ethylenediaminetetraacetic acid (0.01 N Titriplex III) was used for titration until the color turned from red to yellow, resulting in the detection of Fe^{+3} content. The pyritic sulfur content (%) was calculated using Eq. (1) (Açışlı, 2002):

$$Sp=\left(\frac{64.128}{55.847}\right)\times NVF\times\left(\frac{5.5847}{g}\right) \quad (1)$$

where N = normality of Titriplex III solution, V = volume of Titriplex III solution used for titration (mL), F = factor of Titriplex III solution and g = sample weight.

First of all, the properties of the coal sample were expressed. The results of the initial analysis of Sorgun coal are given in Table 1.

Table 1. Sorgun Coal Analysis Results.

Parameter	Original Coal	Dry Coal	Test Method
Humidity %	13.85	--	ASTM D3173 ASTM D3302
Volatile Matter %	29.09	33.76	ASTM D3174
Ash %	25.29	29.35	ASTM D3175
Total Sulfur %	2.21	2.43	ASTM D 4239
Lower calorific value kcal / kg	4009	4742	ISO 1928
Upper calorific value kcal / kg	4246	4928	ASTM D5865

RESULTS AND DISCUSSION

In the current study; desulfurization by oak ash-based extraction liquid of Sorgun coal sample was examined. Figure 2 shows that the total sulfur removal of Sorgun coal

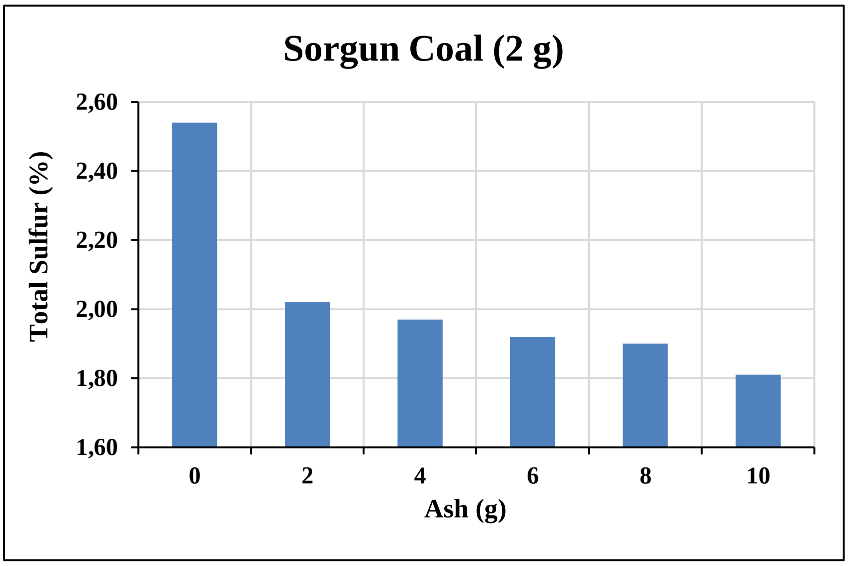

Figure 2. Variation of total desulfurization based on oak ash content

Figure 2 shows the amount of sulfur removed from 2 g of coal reacting with 2 g, 4g, 6 g, 8 g and 10 g of oak ash extraction liquid. Before desulfurization; total sulfur content of Sorgun coal was measured as 2.54%. After desulfurization, total sulfur contents of Sorgun coal were measured as 2.02% (for 2 g), 1.97% (for 4 g), 1.92% (for 6 g), 1.90% (for 8 g) and 1.81% (for 10 g). The highest total sulfur removal was calculated as 28.7%.

In previous studies; a lot of researchers investigated total sulfur removal methods. Singh et al. (2013) researched to removal of total sulfur from Tiru valley coal samples by Pseudoxanthomonas sp. The mean sulfur removal was calculated as 18.26%. Kiani et al. (2014) investigated the bio-desulfurization of Mehr Azin coal with a mixed culture of mesophilic microorganisms. The total sulfur removal was calculated as 50.3%. Wang et al. (2019) investigated desulfurization of coal in H_2O_2 and IL-H_2O_2 mixtures. As a result of the study, total sulfur decreased from 2.15% to 1.21%. The total sulfur removal was calculated as 43.7%.

We compared the pyritic sulfur content of the samples before and after desulfurization with oak ash extraction liquid. 2 g coal samples were treated using five different amounts of oak ash extraction liquid (20 mL, 40 mL, 60 mL, 80 mL and 100 mL) to determine the effect of coal and oak ash contents on the effectiveness of the pyritic desulfurization process. These results show in Figure 3.

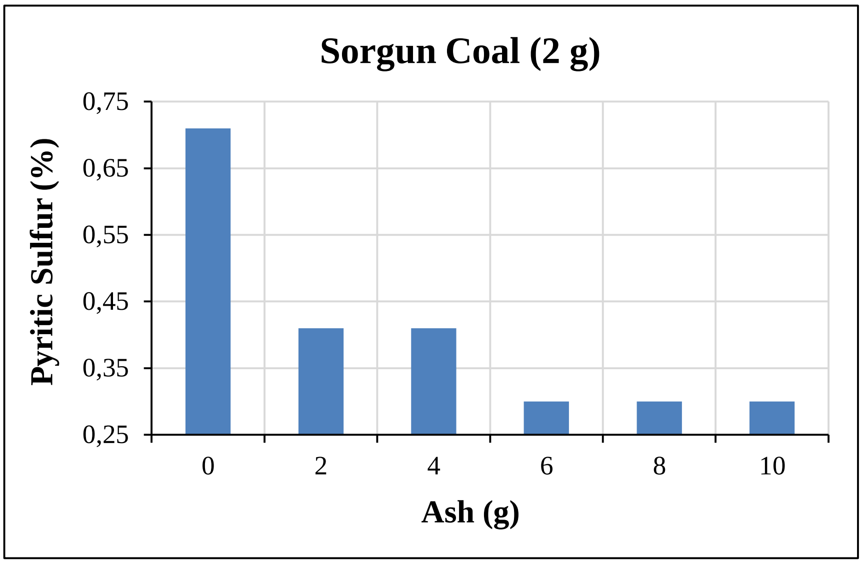

Figure 3. Variation of pyritic desulfurization by oak ash content

Before desulfurization with 2 g, 4 g, 6 g, 8 g and 10 g of oak ash extraction liquid, pyritic sulfur content of 2 g Sorgun coal was measured as 0.71%. After desulfurization, pyritic sulfur contents of Sorgun coal were measured as 0.41% (for 2 g), 0.41% (for 4 g), 0.30% (for 6 g), 0.30% (for 8 g) and 0.30% (for 10 g). The highest pyritic sulfur removal was calculated as 57.7%.

During the last years, researchers investigated various desulfurization methods of coal. Levent et al. (2007) investigated the desulfurization of Artvin/Yusufeli coal with H_2O_2/H_2SO_4 solutions in their study using the Taguchi method. The pyritic sulfur removal was calculated as 56.54%. Zhang et al. (2017) investigated the desulfurization of Inner Mongolia Erdos coal with a novel microwave-enhanced magnetic property processing method. Pyritic sulfur was reduced by 60% after 90 s microwave treatment. Tang et al. (2018) researched desulfurization of 3 gr Xinyu coal and Guxian raw coal utilizing the potassium tert-butoxide/hydrosilane. Pyritic sulfur contents of this coal decreased from 0.21 to 0.02 and 0.40 to 0.06, respectively. It can be said that total sulfur and pyritic sulfur removal results are consistent with the literature.

In order to examine the effect of KOH addition on pyritic desulfurization, 0.02 M 100 mL KOH solution and 2 g Sorgun coal were re-analyzed with oak ash (2 g, 4 g, 6 g, 8 g and 10 g) of different weight. Figure 4 shows these results.

Before desulfurization; pyritic sulfur content of 2 g of Sorgun coal was measured as 0.71%. After desulfurization; pyritic sulfur contents of Sorgun coal were measured as 0.38% (for 2 g oak ash and 0.02 M KOH solution), 0.27% (for 4 g oak ash and 0.02 M KOH solution), 0.27% (for 6 g oak ash and 0.02 M KOH solution), 0.27% (for 8 g oak ash and 0.02 M KOH solution) and 0.27% (for 10 g oak ash and 0.02 M KOH solution). The highest pyritic sulfur removal was calculated as 61.9%. It was observed that the amount of desulfurization was further increased with the addition of KOH. As a result of this analysis, higher removal was obtained due to the chemical contribution.

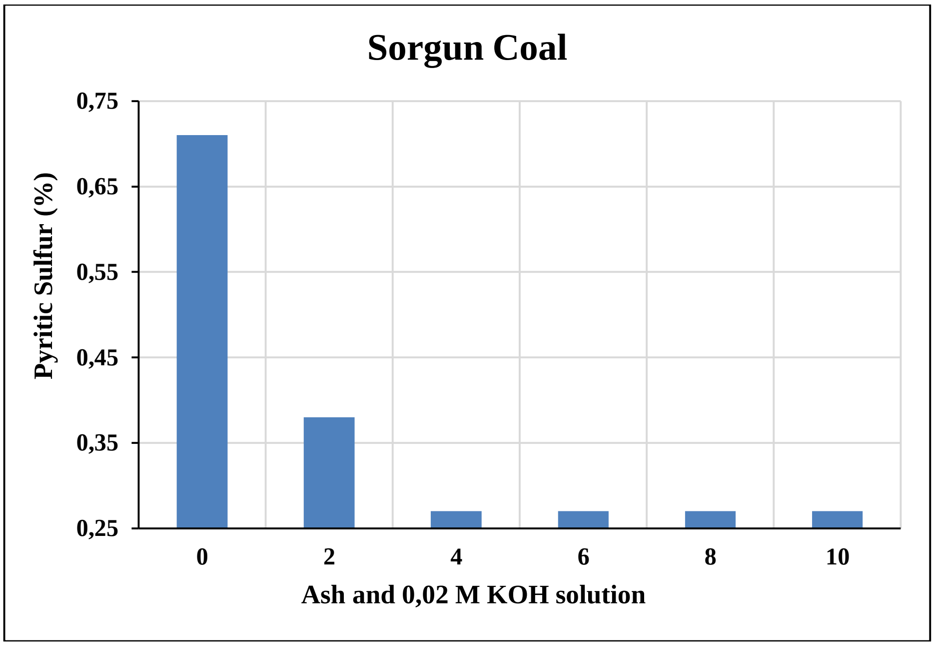

Figure 4. Variation of pyritic desulfurization by mix of oak ash content and 0.02 M KOH

CONCLUSION

In this study; it was aimed to benefit the environment by using waste material for desulfurization process. The oak ash as waste material was used for desulfurization of Sorgun coal. The results obtained from this study are expressed:

- The highest total sulfur and pyritic sulfur removal with oak ash extraction liquids were obtained as 28.7% and 57.7%, respectively.
- The lowest total sulfur and pyritic sulfur removal with oak ash extraction liquids were obtained as 20.5% and 42.3%, respectively.
- The highest and lowest pyritic sulfur removal with oak ash extraction liquids + 0.02 M 100 mL KOH were obtained as 61.9% and 46.5%, respectively.

When the results are examined; it can be said that oak ash can be used instead of physical methods, chemicals or microorganisms for desulfurization process. In addition, it is seen that the analysis results are appropriate to the literature. Since there is no similar study in the literature on the use of waste resources for the desulfurization process, it is clear that this study will contribute to further studies on the desulfurization of coal.

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Conflict of Interest

The article authors declare that there is no conflict of interest between them.

Author's Contributions

The authors declare that they have contributed equally to the article.

REFERENCES

Açışlı Ö, 2002. Desulfurization of Balkaya Lignite at Various Gas Atmospheres. Ataturk University Graduate School of Natural and Applied Sciences, Master Thesis (Printed).

ASTM D2013/D2013M-20, Standard Practice for Preparing Coal Samples for Analysis, ASTM International, West Conshohocken, PA, 2020, https://www.astm.org/Standards/D2013.htm, (Date of access: 22 April 2021).

ASTM D4239-18e1, Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion, ASTM International, West Conshohocken, PA, 2018, https://www.astm.org/Standards/D4239.htm, (Date of access: 22 April 2021).

Boylu F, Karaağaçlıoğlu İE, 2018. Evaluation of Coal Components-Coal Calorific Value Relationship. Journal of Earth Sciences, 39(3): 221-236.

Çelik PA, Aksoy DÖ, Koca S, Koca H, Çabuk A, 2019. The Approach of Biodesulfurization for Clean Coal Technologies: A Review. International Journal of Environmental Science and Technology, 16(4): 2115-2132.

Feng Y, Lu J, Wang J, Mi J, Zhang M, Ge M, Li Y, Zhang Z, Wang W, 2020a. Desulfurization Sorbents for Green and Clean Coal Utilization and Downstream Toxics Reduction: A Review and Perspectives. Journal of Cleaner Production, 273: 123080.

Feng Y, Wang J, Hu Y, Lu J, Zhang M, Mi J, 2020b. Microwave Heating Motivated Performance Promotion and Kinetic Study of Iron Oxide Sorbent for Coal Gas Desulfurization. Fuel, 267: 117215.

Kiani MH, Ahmadi A, Zilouei H, 2014. Biological Removal of Sulphur and Ash from Fine-Grained High Pyritic Sulphur Coals Using A Mixed Culture of Mesophilic Microorganisms. Fuel, 131: 89-95.

Kumar A, Singh A, Singh P, Singh A, Saikia BK, Kumar A, 2019. Desulfurization of Giral Lignite of Rajasthan (Western India) Using Burkholderia sp. GR 8–02. International Journal of Coal Preparation and Utilization, 1-17.

Levent M, Kaya Ö, Kocakerim M, Yiğit V, Küçük Ö, 2007. Optimization of Desulphurization of Artvin–Yusufeli Lignite with Acidic Hydrogen Peroxide Solutions. Fuel, 86(7-8): 983-992.

Li W, Tang Y, 2014. Sulfur Isotopic Composition of Superhigh-Organic-Sulfur Coals from The Chenxi Coalfield, Southern China. International Journal of Coal Geology, 127: 3-13.

Liu T, Hou JH, Peng YL, 2017. Biodesulfurization from The High Sulfur Coal with A Newly Isolated Native Bacterium, Aspergillus sp. DP06. Environmental Progress & Sustainable Energy, 36(2): 595-599.

Liu F, Lei Y, Shi J, Zhou L, Wu Z, Dong Y, Bi W, 2020. Effect of Microbial Nutrients Supply on Coal Biodesulfurization. Journal of Hazardous Materials, 384: 121324.

Longjun X, Cai-Xi C, 2007. Effect of Nitric Acid Pretreation on Organic Sulfur Removal of Coal by 1-phrpyl Alcohol. Coal Conversion, 30: 76-79.

Meshroghli S, Yperman J, Jorjani E, Carleer R, Noaparast M, 2015. Evaluation of Microwave Treatment on Coal Structure and Sulfur Species by Reductive Pyrolysis-Mass Spectrometry Method. Fuel Processing Technology, 131: 193-202.

Ning X, Xiuxiang T, 2015. Changes in Sulfur Form During Coal Desulfurization with Microwave: Effect on Coal Properties. International Journal of Mining Science and Technology, 25(3): 435-438.

Singh PK, Singh AL, Kumar A, Singh MP, 2013. Control of Different Pyrite Forms on Desulfurization of Coal with Bacteria. Fuel, 106: 876-879.

Singh AK, Kumar A, Singh PK, Singh AL, Kumar A, 2018. Bacterial Desulphurization of Low-rank Coal: A Case Study of Eocene Lignite of Western Rajasthan, India. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 40(10): 1199-1208.

Tang L, Wang S, Zhu X, Guan Y, Chen S, Tao X, He H, 2018. Feasibility Study of Reduction Removal of Thiophene Sulfur in Coal. Fuel, 234: 1367-1372.

Tang L, Fan H, Chen S, Tao X, He H, Zhu X, 2020. Investigation on The Synergistic Mechanism of Coal Desulfurization by Ultrasonic with Microwave. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 42(20): 2516-2525.

Wang L, Jin G, Xu Y, 2019. Desulfurization of Coal Using Four Ionic Liquids with $[HSO_4]^-$. Fuel, 236: 1181-1190.

Wang M, Shen Y, Hu Y, Kong J, Wang J, Chang L, 2020. Effect of Pre-desulfurization Process on The Sulfur forms and Their Transformations During Pyrolysis of Yanzhou High Sulfur Coal. Fuel, 276: 118124.

Xia W, Xie G, 2017. A Technological Review of Developments in Chemical-related Desulfurization of Coal in the Past Decade. International Journal of Mineral Processing, 161: 65-71.

Ye J, Zhang P, Zhang G, Wang S, Nabi M, Zhang Q, Zhang H, 2018. Biodesulfurization of High Sulfur Fat Coal with Indigenous and Exotic Microorganisms. Journal of Cleaner Production, 197: 562-570.

Yong-liang X, Yang L, Yun-Chuan B, Meng-Lei C, Lan-Yun W, 2020. Review on The Ionic Liquids Affecting The Desulfurization of Coal by Chemical Agents. Journal of Cleaner Production, 284: 124788.

Zhang B, Yan G, Zhao Y, Zhou C, Lu Y, 2017. Coal Pyrite Microwave Magnetic Strengthening and Electromagnetic Response in Magnetic Separation Desulfurization Process. International Journal of Mineral Processing, 168: 136-142.