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Effect of Conventional and Microwave Heating on Organic Sulphur Desulfurization from Coal Using Some Metal Salts

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Abstract: A novel experiment was carried out for the removal of organic sulphur by the electron transfer process. In these experiments, the effect of conventional and microwave heating were investigated on the desulfurization of organic sulphur. The aim of the study was formed soluble metal-organic sulfur bonds using Pd^{+2}, Sn^{2+} and Sb^{3+} metal ions of variable valence state. In this way, it was tried to create a mechanism that cleavage the C-S bonds. Desulfurization occurs by breaking the aliphatic sulfur bonds of metal ions with high negative oxidation potential. As a result of the studies, 24.30% of total sulfur was removed with Pd^{2+} ion. In microwave heating, it was determined that higher organic sulfur was removed in less leaching times.

Key words : Electron transfer process, Desulfurization, Organic sulphur, Coal, Microwave

Bazı Metal Tuzlarıyla Kömürden Organik Sülfürün Desülfürizasyonuna Klasik ve Mikrodalga Isıtmanın Etkisi

Öz: Bu çalışmada, organik kükürdün elektron transfer işlemi ile uzaklaştırılması araştırılmıştır. Deneylerde, organik kükürdün uzaklaştırılmasında klasik ve mikrodalga ısıtma teknikleri kullanılmıştır. Çalışmada farklı değerlikli Pb, Sn ve Sb metal iyonları kullanılarak çözünebilir metal-organik kükürt bağlarının oluşturulması amaçlanmıştır. Bu sayede, C-S bağlarını parçalayan bir mekanizma oluşturulmaya çalışılmıştır. Böylece, yüksek negatif oksidasyon potansiyeline sahip metal iyonlarının alifatik sülfür bağlarının kırılmasıyla kükürt uzaklaştırma sağlanabilmiştir. Çalışmaların sonucunda toplam sülfürün %24.30'u Pd^{2+} iyonu ile uzaklaştırılmıştır. Ayrıca, mikrodalga ısıtmada, daha kısa zamanda daha yüksek organik sülfürün uzaklaştırıldığı belirlenmiştir.

Anahtar Kelimeler: Elektron transfer yöntemi, Desülfürizasyon, Organik kükürt, Kömür, Mikrodalga

1. Introduction

To increase the calorific values of our lignite, washing processes are generally carried out in coal preparation facilities and non-coal materials are tried to be removed by physical methods. In this way, the ash content of our low-quality lignite is reduced and their calorific values are increased, making them usable in thermal power plants and in houses for heating purposes. However, the utilization of high sulphur coals has been a great concern, especially for combustion processes because of the emission of SO_2 to the atmosphere which causes severe air pollution and formation of acid rain [1, 2].

Sulphur in coal occurs in the forms of elemental, sulfate, sulphite and organic sulphur as four

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groups [3]. The most important sulphur forms in coal are sulphides (pyritic) and organic sulphides. Sulfide minerals defined as sulfites are generally pyrite (FeS_2) and marcasite (FeS_2) type minerals. Such sulphur sources can be removed from coal by gravity, magnetic or physicochemical and chemical methods, providing a reasonable degree of attenuation [4-6]. With these methods, only 10-40% of the total sulphur is removed. Most of the remaining sulfur is organic sulfur. Organic sulfur is molecularly linked to coal as part of coal. Therefore, it is very much important to understand the precise nature and type of organic sulphur compounds present in coal as these are prerequisites for efficient desulphurization. Organic sulfur is generally accepted in 3 classes. These; aliphatic sulphur, aromatic sulphur, and thiophene sulphur [7]. Separate of these sulfurs from coal by physical methods are quite difficult. A vast majority of the methods are concerned with chemical processes. Some chemicals used in these methods are hydrogen peroxide, sulfuric acid, nitric acid, peracetic acid, potassium permanganate, sodium dichromate, methanol ethanol, acetic acid, hydrochloric acid, hydroiodic acid, potassium hydroxide, and sodium hydroxide [8-33].

Another chemical method is the electron transfer method. A study applied the electron transfer method by using coals that have completely removed the inorganic sulfur to remove the organic sulfur contained in the coal [34]. In a study, the researcher used ferrocyanide ions as an electron transfer reagent. The researcher stated that more than 30% of organic sulfur can be removed. In another study, after the oxidation process at different temperatures, both in the raw coal and with mercury-treated high-sulphur India Meghalaya coals used the electron transfer method [35]. The highest rate of desulphurization was obtained as 19.17% in the presence of naphthalene in coal, while it was realized as 17.78% in the coal threatened with mercury. By applying this method, 27.38% of the organic sulphur could be removed in the raw coal, while this ratio was 28.45% in the mercury treated coal. In another study, researchers examined the effect of mercury on sulfur removal using the same coal [36]. They determined that mercury both accelerates oxidation and is an effective substance in sulfur removal. In a similar study, metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Sn^{2+}, and Sb^{3+}) used the separation of C-S bonds investigated the formation of soluble metal-organic sulphur bonds [2]. As a result of their research, they were able to remove 9.4% of the total organic sulphur with Sb^{3+}. They suggested the following mechanism of organic sulfur removal in their work (Eq 1-3).

Step 1 $$M^{n+} + x(Naphtlane) \rightarrow \underbrace{(Naphtlane)_x M^{(n+x)+}}_{I} \quad (1)$$

Step 2 $$x(R-S-R) + I \rightarrow \underbrace{x(R-S)^-}_{II} + xR + x(Naphtlane) + M^{n+} \quad (2)$$

Step 3 $$I + II \rightarrow (R-R) + x(Naphtlane) + \underbrace{(M_2S_n)}_{III} \quad (3)$$

The interaction of metal ion with naphthalene forms naphthalene radical anion, I (step 1) which subsequently reacts with organic sulphur compound forming II (step 2). The compound II might be soluble in the medium. The radical anion I may further react with the compound II and form insoluble metal sulphide III (step 3) [2].

In another study similarly leached with peracetic acid ($C_2H_4O_3$) in the presence of metal ions to remove sulfur from coal [37]. During these processes, Cu^{2+}, Ni^{2+}, Co^{2+}, Sn^{2+}, Pd^{2+}, Sb^{3+} used metal ions. They achieved the highest sulfur removal with Pd^{2+} ion. After 4 hours of leaching, they removed 32.32% of organic sulfur.

Unlike these studies, some studies were used ultrasonic waves and microwave energy to remove organic sulfur. The positive effect of microwave irradiation as a pretreatment for subsequent desulfurization with peroxyacetic acid has been reported in an earlier published work [38]. In this way, they removed the maximum 86.6% of total sulfur and 35% of organic sulfur. Also, another researcher tried to remove sulfur from coal using microwave energy [39]. In their studies, they pre-washed with HNO_3 and removed sulfur from the coals by microwave. Thus, 47.1% of the total sulfur was removed. The other researchers tried to remove sulfur from Çayırhan and Gediz coals by the oxidation method [19]. For this, they leached the coal with peracetic acid (peroxyacetic acid) ($C_2H_4O_3$). They used an ultrasonic wave to speed up the reaction process. In this way, they removed more sulfur.

In this study, the electron transfer process was used for the desulphurization of organic sulphur from Turkish coals. Pd^{2+}, Sn^{2+} and Sb^{3+} metal ions were used in this method. The work was done with both classical heating and microwave heating. Each metal ion was worked with both conventional heating and microwave heating. Also, the effect of heating parameters had been determined.

2. Experimental Methods

2.1. Materials

The sample was obtained from the Tuncbilek coal mine in Turkey. Proximate and ultimate analysis of the sample, as well as the total, pyritic and sulfate forms of sulphur are shown in Table 1. Different forms of sulfur were determined using ISO methods 334 and 157 [40, 41]. According to the results of the analysis, it was determined that the coal sample to be used in the study contains 3.05% of this amount was organic sulphur.

Table 1. The results of the coal analysis

The Coal Analysis		
Total Moisture	%	1.60
Ash	%	53.04
Volatile Matter	%	25.84
Fixed Carbon	%	19.52
Lower Heating Value	Kcal/kg	3,115
Elementary Analysis		
Carbon	%	30.33
Hydrogene	%	2.58
Azote	%	0.92
Oxygen	%	6.07
Total Sulphur	%	3.89
Organic Sulphur	%	3.05
Pyrite Sulphur	%	0.29
Sulphate Sulphur	%	0.55

2.2 Preparation of Coal

Coal samples were reduced to below 0.5 mm with the jaw crusher and hammer mill to increase the surface area of the coal grains. These samples were used in organic desulphurization experiments.

2.3 Preparation of Metal Salts and Treatment of Coal

Experiments were carried out using the coal samples prepared above. $PdCl_2$, $SnCl_2$, and $SbCl_3$ metal salts were used in the studies. we have proposed the following mechanism for the removal of sulphur from organic sulphur compound (Eq. 4)

$$(R-S-R)+M^{n+} \rightarrow (R-R)+M_2S_n \tag{4}$$

Organic desulphurization experiments were performed using both conventional heating and microwave heating techniques using the following parameters (Table 2). Samples were prepared in advance for experiments in 250 cc beakers.

In the conventional heating method, a magnetic stirrer with heating was used to heat the solution. In microwave heating techniques, Lab-Kits brand MW-ER-02 model ultrasonic/microwave reactor was used. Microwave power was used to heat the solution. In these experiments, ultrasonic waves were used for mixing. The solid materials were filtered out, washed with distilled water and finally, the solid materials were dried in an oven at 100 °C for 2 h. The sulphur removal rate (SRR) was calculated by sulphur analysis as follows (Equal 1).

$$\text{Sulphur removal rate (\%)} = \frac{S_F - S_C}{S_F} x100 \tag{5}$$

where SF: sulpfur content of feed (%), SC: sulphur content of coal after experiment (%)

Table 2. Conventional and microwave heating test parameters.

Heating Process	Independent variable	Symbol	Minimum	Maximum
Conventional Heating	Chemical concentration (M)	KK	0.1	0.3
	Reaction Temperature (°C)	S	30	90
	Time (m)	Z	30	120
	Mixing Speed (rpm)	KH	600	1350
	Solid Ratio (%)	KO	5	20
Microwave Heating	Chemical concentration (M)	KK	0.1	0.3
	Time (m)	Z	5	20
	Microwave power (W)	MG	400	1200
	Solid Ratio (%)	KO	5	20

2.4 Statistical Analysis

Statistical methods are used to analyze the data gathered to obtain information from observations and to draw correct meanings. The purpose of statistical experiment design is to obtain maximum meaningful data with minimum time, resource and expenditure. Today, statistical analysis methods are used in almost every branch of science. In this study, statistical analysis methods were used.

In this study, response surface methods, one of the statistical experimental design methods, were used. In the experiments, the experiment program prepared using the Box-Behnken design technique was used. Experimental design and statistical analyzes were done using Minitab 16 statistical experiment design program. With selected independent parameters and levels, 46 experiments (6 central points) in Conventional heating and 27 (3 central points) in microwave heating were determined. The experimental set prepared for conventional heating was given in Table 3 and the experimental set prepared for microwave heating was given in Table 4. The tables show the minimum levels -1, the maximum levels 1, and the intermediate levels 0. With the data obtained as a result of the experiments, 2^{nd}-degree models that define the removal of sulfur rate have been produced.

Table 3. Experimental coding for conventional heating.

Exp. No	Independent variable					Exp. No	Independent variable				
	KK	S	Z	KH	KO		KK	S	Z	KH	KO
1	0	0	0	0	0	**24**	0	0	0	0	0
2	0	1	0	1	0	**25**	0	0	0	0	0
3	0	-1	0	0	1	**26**	1	0	0	-1	0
4	0	-1	0	0	-1	**27**	0	0	0	0	0
5	1	0	1	0	0	**28**	-1	0	0	-1	0
6	0	1	1	0	0	**29**	0	0	0	0	0
7	0	-1	0	-1	0	**30**	1	0	0	0	-1
8	0	0	0	-1	1	**31**	0	0	1	0	-1
9	0	0	1	1	0	**32**	-1	0	0	1	0
10	0	-1	1	0	0	**33**	0	0	1	-1	0
11	-1	1	0	0	0	**34**	-1	0	1	0	0
12	0	1	0	-1	0	**35**	0	0	-1	-1	0
13	1	0	-1	0	0	**36**	0	0	0	1	-1
14	0	0	0	1	1	**37**	0	0	0	-1	-1
15	0	0	1	0	1	**38**	-1	-1	0	0	0
16	1	1	0	0	0	**39**	0	-1	-1	0	0
17	0	0	-1	1	0	**40**	-1	0	0	0	1
18	0	0	-1	0	-1	**41**	0	1	-1	0	0
19	0	1	0	0	1	**42**	1	0	0	1	0
20	0	-1	0	1	0	**43**	-1	0	0	0	-1
21	0	0	-1	0	1	**44**	0	0	0	0	0
22	0	1	0	0	-1	**45**	1	-1	0	0	0
23	1	0	0	0	1	**46**	-1	0	-1	0	0

Table 4. Experimental coding for microwave heating

Exp. No	Independent variable				Exp. No	Independent variable			
	KK	Z	MG	KO		KK	Z	MG	KO
1	0	1	-1	0	**15**	-1	0	-1	0
2	-1	0	0	1	**16**	-1	1	0	0
3	-1	0	1	0	**17**	-1	-1	0	0
4	1	1	0	0	**18**	0	0	1	1
5	0	0	0	0	**19**	1	0	-1	0
6	1	-1	0	0	**20**	-1	0	0	-1
7	0	0	1	-1	**21**	0	1	1	0
8	0	-1	-1	0	**22**	1	0	1	0
9	1	0	0	1	**23**	0	-1	0	-1
10	0	0	0	0	**24**	0	1	0	1
11	0	-1	1	0	**25**	0	0	-1	1
12	0	0	0	0	**26**	0	1	0	-1
13	0	0	-1	-1	**27**	0	-1	0	1
14	1	0	0	-1					

3. Results and Discussion

3.1. Removal of Sulfur by Conventional Heating

The results of sulphur removal experiments using conventional heating methods were given in Table 5. Table 5 shows the results for all 3 metal salts.

When a general assessment of the results obtained was made, the optimum sulfur removal rate for $PdCl_2$ and $SnCl_2$ metal salt in Experiment 16 (KK = 0.3 M; S = 90 °C; Z = 75 min; KH = 975 rpm;

KO= 12.5%) was obtained as 22.07% and 5.25% respectively. For $SbCl_3$ metal salt, it was obtained as 7.19% in Experiment 23 (KK = 0.3 M; S= 60 °C; Z= 75 min; KH= 975 rpm; KO= 20%).

Table 5. Conventional heating test results.

Sıra No	SRR			Sıra No	SRR			Sıra No	SRR		
	$PdCl_2$	$SnCl_2$	$SbCl_3$		$PdCl_2$	$SnCl_2$	$SbCl_3$		$PdCl_2$	$SnCl_2$	$SbCl_3$
1	15,83	3,23	5,66	**17**	18,15	3,69	3,91	**32**	15,64	2,20	4,26
2	17,96	4,08	3,83	**18**	13,69	2,50	3,09	**33**	17,37	3,75	5,04
3	20,92	2,10	6,20	**19**	17,85	2,62	6,54	**34**	19,22	2,26	5,14
4	16,69	3,42	3,28	**20**	15,58	3,10	4,55	**35**	20,95	3,47	6,15
5	20,82	4,05	6,08	**21**	16,51	3,68	2,94	**36**	17,73	3,71	5,01
6	19,48	4,61	5,30	**22**	19,85	3,83	4,11	**37**	17,31	1,97	5,89
7	15,05	2,36	4,93	**23**	21,59	3,47	**7,19**	**38**	9,99	1,34	3,53
8	19,69	2,75	3,35	**24**	15,83	3,23	5,66	**39**	15,39	2,84	4,56
9	18,85	4,02	4,67	**25**	15,83	3,23	5,66	**40**	16,59	3,70	4,41
10	17,19	4,12	5,43	**26**	21,65	3,27	6,57	**41**	18,22	2,82	4,38
11	15,28	2,32	3,85	**27**	15,83	3,23	5,66	**42**	18,77	3,48	6,70
12	19,85	3,87	6,27	**28**	12,62	2,51	4,58	**43**	13,25	3,97	3,97
13	20,69	4,82	4,20	**29**	15,83	3,23	5,66	**44**	15,83	3,23	5,66
14	15,77	2,45	4,48	**30**	20,77	4,73	6,91	**45**	20,60	3,14	5,97
15	16,34	1,87	6,33	**31**	16,50	3,76	6,39	**46**	13,49	1,75	2,22
16	**22,07**	**5,25**	7,11								

According to these results, it was observed that the desire to replace Pd^{2+} ions with sulfur was higher than that of other ions. The regression model coefficients obtained using Table 5 were given in Table 6. In this part, the highest correlation coefficient was obtained in $PdCl_2$ metal salt.

Table 6. Second order model equations for sulfur removal rate.

Metal salt	Regression Model	R^2
$PbCl_2$	$-12,8464+118,34x\mathbf{KK}+0,157x\mathbf{S}+0,04x\mathbf{Z}+1,7x10^{-3}x\mathbf{KH}+0,8133x\mathbf{KO}+30,5x\mathbf{KK^2}+4,83x10^{-4}x\mathbf{S^2}+2,65x10^{-4}x\mathbf{Z^2}+4,065x10^{-6}x\mathbf{KH^2}+9,5x10^{-3}x\mathbf{KO^2}-0,268x\mathbf{KK}x\mathbf{S}-0,388x\mathbf{KK}x\mathbf{Z}-4,3x10^{-2}x\mathbf{KK}x\mathbf{KH}-0,997x\mathbf{KK}x\mathbf{KO}-1,815x10^{-4}x\mathbf{S}x\mathbf{Z}-4,42x10^{-5}x\mathbf{S}x\mathbf{KH}-5,56x10^{-3}x\mathbf{S}x\mathbf{KO}+4,46x10^{-5}x\mathbf{Z}x\mathbf{KH}-2,23x10^{-3}x\mathbf{Z}x\mathbf{KO}-2,67x10^{-4}x\mathbf{KH}x\mathbf{KO}$	76,39
$SnCl_2$	$-7,53497+11,5525x\mathbf{KK}+1,53x10^{-2}x\mathbf{S}+6,02x10^{-2}x\mathbf{Z}+3,75x10^{-3}x\mathbf{KH}+0,469x\mathbf{KO}-11,04x\mathbf{KK^2}-1,9x10^{-5}x\mathbf{S^2}-5,144x10^{-6}x\mathbf{Z^2}-5x10^{-7}x\mathbf{KH^2}-1,52x10^{-3}x\mathbf{KO^2}+0,0975x\mathbf{KK}x\mathbf{S}-0,072x\mathbf{KK}x\mathbf{Z}-6,67x10^{-5}x\mathbf{KK}x\mathbf{KH}-0,157x\mathbf{KK}x\mathbf{KO}+9,63x10^{-5}x\mathbf{S}x\mathbf{Z}-2,22x10^{-7}x\mathbf{S}x\mathbf{KH}-2,22x10^{-3}x\mathbf{S}x\mathbf{KO}-1,48x10^{-5}x\mathbf{Z}x\mathbf{KH}-2,69x10^{-3}x\mathbf{Z}x\mathbf{KO}-8,89x10^{-5}x\mathbf{KH}x\mathbf{KO}$	55,87
$SbCl_3$	$-0,52+7,51x\mathbf{KK}+0,1006x\mathbf{S}-8,19x10^{-3}x\mathbf{Z}+5,93x10^{-4}x\mathbf{KH}+2,37x10^{-3}x\mathbf{KO}+1,75x\mathbf{KK^2}-9,72x10^{-5}x\mathbf{S^2}-1,399x10^{-4}x\mathbf{Z^2}-1,458x10^{-6}x\mathbf{KH^2}-6,029x10^{-3}x\mathbf{KO^2}-0,055x\mathbf{KK}x\mathbf{S}+0,0556x\mathbf{KK}x\mathbf{Z}-4x10^{-4}x\mathbf{KK}x\mathbf{KH}+0,1x\mathbf{KK}x\mathbf{KO}-3,67x10^{-4}x\mathbf{S}x\mathbf{Z}-2,22x10^{-5}x\mathbf{S}x\mathbf{KH}-0,0011x\mathbf{S}x\mathbf{KO}+2,963x10^{-5}x\mathbf{Z}x\mathbf{KH}+1,489x10^{-3}x\mathbf{Z}x\mathbf{KO}+8,978x10^{-5}x\mathbf{KH}x\mathbf{KO}$	58,22

3.1.1. Effect of Conventional Heating Variables on SRR

To obtain a better understanding of the results, the predicted models are presented in Fig. 1 (A–E) as 2D (two dimensional) response surface plots. The figures show the relationship between one variable of conventional heating and sulphur removal rate (%) of coal at the center level of the other four variables.

Fig. 1A shows the effect of chemical concentration on SRR at the center level of other variables. The effect of chemical concentration on SRR was positive. The sulfur removal rate increased as the chemical concentration increased. The highest sulfur removal rate was obtained at a chemical concentration of 0.3 M. This was an expected situation. C-S bonds were broken by bonding more metal salt with more sulfur. Fig. 1B shows the effect of reaction temperature on SRR at the center level of other variables. Similarly, the effect of reaction temperature on SRR was positive. As the reaction temperature increased, the sulfur removal rate also increased. Chemical reactions are faster at higher temperatures.

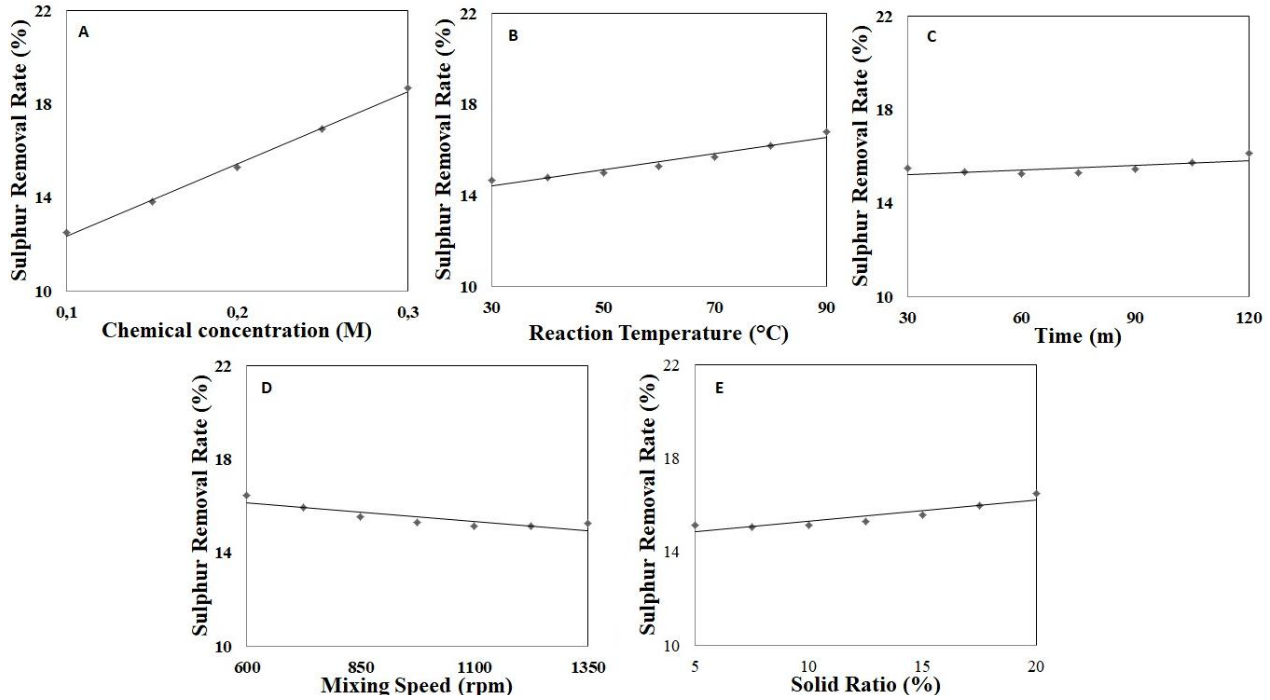

Figure 1. Effect of conventional heating variables on SRR

However, if we look at the slope of the curve, we can say that its effect is lower than the chemical concentration. Fig. 1C shows the effect of time on SRR at the center level of other variables. The reaction time was a very low positive effect on SRR. In other words, most of the chemical reaction occurred in the first 30 minutes. Fig. 1D shows the effect of mixing speed on SRR at the center level of other variables. In contrast to other variables, the mixing speed had a negative effect. The lower sulfur removal rate was obtained at high mixing speeds. Fig. 1E shows the effect of the solid ratio on SRR at the center level of other variables. The solid ratio was also rarely effective on SRR. A small amount of positive effect was seen on SRR.

3.2. Removal of Organic Sulfur by Microwave Heating

The results of sulfur removal experiments using the microwave heating method were given in Table 7. Table 7 shows the results for all 3 metal salts.

When a general assessment of the results obtained was made, the optimum sulfur removal rate for $PdCl_2$ metal salt in Experiment 9 (KK= 0.3 M; Z= 12.5 min; MG= 800 W; KO= 20%) was obtained as 24.30%. For $SnCl_2$ and $SbCl_3$ metal salts, it were obtained as 5.83% and 10.21% in Experiment 22 (KK= 0.3 M; Z= 12.5 min; MG= 1200 W; KO= 12.5%). According to these results, it was observed that the desire to replace Pd^{2+} ions with sulfur was higher than that of other ions.

Table 7. Microwave heating test results.

Sıra No	SRR			Sıra No	SRR			Sıra No	SRR		
	$PdCl_2$	SnCl2	SbCl3		$PdCl_2$	SnCl2	SbCl3		$PdCl_2$	SnCl2	SbCl3
1	16,94	3,32	6,58	**10**	17,91	4,19	7,73	**19**	19,69	2,94	9,63
2	14,14	2,55	4,91	**11**	18,24	5,61	6,77	**20**	12,78	4,01	4,36
3	12,99	4,46	4,88	**12**	17,91	4,19	7,73	**21**	20,47	4,70	7,15
4	21,50	4,93	9,54	**13**	16,23	4,21	7,56	**22**	24,07	**5,83**	**10,21**
5	17,91	4,19	7,73	**14**	20,14	5,32	10,02	**23**	16,58	5,12	5,74
6	18,16	1,83	6,83	**15**	12,92	2,56	6,23	**24**	20,13	2,78	8,23
7	16,27	5,11	8,69	**16**	19,52	4,10	4,64	**25**	17,03	2,28	7,82
8	18,20	3,69	6,82	**17**	15,31	2,96	3,97	**26**	18,79	2,73	7,39
9	**24,30**	2,92	6,11	**18**	21,00	4,70	7,90	**27**	19,45	3,67	7,81

The regression model coefficients obtained using Table 7 were given in Table 8. In this part, the highest correlation coefficient was obtained in $PdCl_2$ metal salt.

Table 8. Second order model equations for sulfur removal rate for microwave heating.

Metal iyon	Regresyon Modeli	R^2
$PbCl_2$	$13,6635+20,58x\mathbf{KK}-0,362x\mathbf{Z}-4,52x10^{-3}x\mathbf{MG}-0,104x\mathbf{KO}-46,54x\mathbf{KK^2}+0,013x\mathbf{Z^2}-4,46x10^{-6}x\mathbf{MG^2}-2,96x10^{-4}x\mathbf{KO^2}+1,73x10^{-15}x\mathbf{KKxZ}+2,78x10^{-2}x\mathbf{KK}x\mathbf{MG}+0,663x\mathbf{KK}x\mathbf{KO}+3,33x10^{-4}x\mathbf{ZxMG}-8,89x10^{-3}x\ \mathbf{Z}x\mathbf{KO}+3,332x10^{-4}x\mathbf{MG}x\mathbf{KO}$	84,69
$SnCl_2$	$2,229+12,8417x\mathbf{KK}-4,99x10^{-2}x\mathbf{Z}-2,45x10^{-3}x\mathbf{MG}+5,79x10^{-2}x\mathbf{KO}-37,33x\mathbf{KK^2}-8,9x10^{-3}x\mathbf{Z^2}+7,84x10^{-7}x\ \mathbf{MG^2}-4,44x10^{-3}x\mathbf{KO^2}+0,667x\mathbf{KKxZ}+6,3x10^{-3}x\mathbf{KK}x\mathbf{MG}-0,663x\mathbf{KK}x\mathbf{KO}+8,33x10^{-5}x\mathbf{ZxMG}+4,44x10^{-3}x\ \mathbf{Z}x\mathbf{KO}+8,33x10^{-5}x\mathbf{MG}x\mathbf{KO}$	76,05
$SbCl_3$	$3,1945+29,1833x\mathbf{KK}-4,4x10^{-2}x\mathbf{Z}-4,24x10^{-3}x\mathbf{MG}+0,1695x\mathbf{KO}-54,208x\mathbf{KK^2}-5,2x10^{-3}x\mathbf{Z^2}+2,08x10^{-6}x\ \mathbf{MG^2}-2,99x10^{-3}x\mathbf{KO^2}+0,663x\mathbf{KKxZ}+6,25x10^{-3}x\mathbf{KK}x\mathbf{MG}-0,663x\mathbf{KK}x\mathbf{KO}+8,25x10^{-53}x\ \mathbf{ZxMG}+4,44x10^{-5}x\mathbf{Z}x\mathbf{KO}+8,33x10^{-7}x\mathbf{MG}x\mathbf{KO}$	78,63

3.2.1. Effect of Microwave Heating Variables on SRR

To obtain a better understanding of the results, the predicted models are presented in Figure 2 (A–D) as 2D (two dimensional) response surface plots. The figures show the relationship between one variable of microwave heating and sulphur removal rate (%) of coal at the center level of the other three variables.

Figure 2A shows the effect of chemical concentration on SRR at the center level of other variables. As with conventional heating, chemical concentration had a positive effect. The sulfur removal rate increased as the chemical concentration increased. The highest sulfur removal rate was obtained at a chemical concentration of 0.3 M. Figure 2B shows the effect of time on SRR at the center level of other variables. Similarly, reaction time had a positive effect. More sulfur was removed in a shorter time than conventional heating. Most of the chemical reactions in microwave heating occurred in the first 5 minutes. Figure 2C shows the effect of microwave power on SRR at the center level of other variables. The effect of microwave power was positive. More sulfur was removed at higher microwave power. Figure 2D shows the effect of the solid ratio on SRR at the center level of other variables. As in conventional heating, the solid rate had a positive effect on SRR.

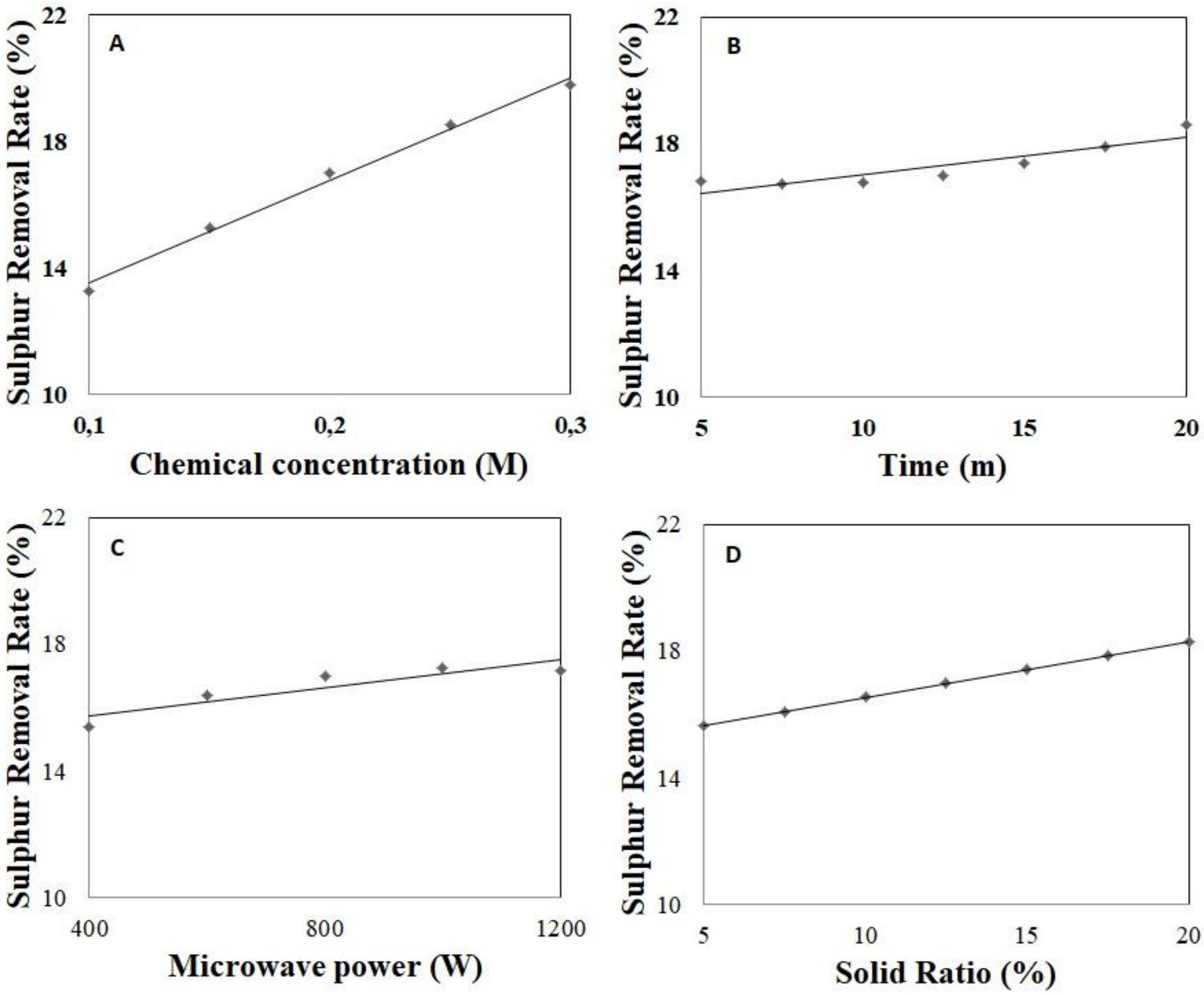

Figure 2. Effect of Microwave heating variables on SRR.

4. Conclusion

In this study, the electron transfer process was used for the desulphurization of organic sulphur. Metal ions (Pd^{2+}, Sn^{2+}, and Sb^{3+}) were utilized for this purpose. Both classical and microwave heating were used in studies to understand the effect of microwave heating. A three-level Box–Behnken factorial design combined with a response surface methodology was used for modeling and optimizing operation parameters of conventional heating (chemical concentration, reaction temperature, time, mixing speed, and solid ratio) and microwave heating (chemical concentration, time, microwave power, and solid ratio), to remove sulfur from coal.

As a result of studies, 22.07% of total sulpfur was removed with Pb^{2+} ion by the conventional heating method. Likewise, by using Sn^{2+} and Sb^{3+} ions, it removed 5.25% and 7.19% of total sulpfur, respectively. The highest sulfur removal rate was obtained using $PbCl_2$ metal salt. In the microwave heating method, 24.30% sulfur with Pb ion, 5.83% with Sn ion, and 10.21% sulfur with Sb ion were removed. Higher results were obtained with microwave heating. However, there is another point that needs attention. By using microwave heating, higher SRR was obtained at a lower time. For example, in a 5-minute process, approximately 17% SRR was achieved. In the conventional heating method, the sulfur removal rate was reached 15% in 30 minutes. This time difference provides a very significant energy saving. Sulfur removal rates obtained in tests with both devices were not very high. However, it had been shown that these methods can be used in organic sulfur removal. With the detailed studies carried out, the effect of the parameters of the devices was also revealed. Thus, it will lead to studies that will contribute economically.

References

[1]. Özgen, S., Sezgin, Ö, "Studies on Hydrocyclone to Produce Clean Coal from Turkish Lignite Tailings (Tunçbilek/Kütahya and Soma/Manisa)", El-Cezerî Journal of Science and Engineering, 2014, 1(1): 12-18.
[2]. Borah, D., Baruah, M.K., "Electron Transfer Process Part 1. Removal of Organic Sulphur from High Sulphur Indian Coal", Fuel, 1999, 78: 1083-1088.
[3]. J. Chakrabarti, "Analytical procedures for sulfur in coal desulfurization products C.J. Karr (Eds) Analytical Methods for Coal and Coal Products", Academic Press, 1978, New York 279–323.
[4]. Leonard, J.W., "Coal Preparation", The American Institute of Mining and Metallurgy and Petroleum Engineers, 1979.
[5]. Wills, B.A., "Mineral Processing Technology", Pregamon Press, Oxford, 1988, 456p.
[6]. Göktepe, F., "Kömür Flotasyonunda Bakteri İlavesinin Piritik Kükürt Uzaklaştırmasına Etkisi", Türkiye 13. Kömür Kongresi, Zonguldak, 125-132, 2002.
[7]. Qi, Y., Li, W., Chen, H., Li, B., "Desulfurization of Coal Through Pyrolysis in a Fluidized-Bed Reactor under Nitrogen and 0.6% O_2-N_2 Atmosphere", Fuel, 2004, 83: 705-712.
[8]. Palmer, SR., Hippo, EJ., Dorai, XA., "Selective oxidation pretreatment for enhanced desulfurization of coal", Fuel, 1995, 74(2): 193-200.
[9]. Zhao, J.L., Zhang, Y.Y., Chen, Q., Fu, Q., "Study on Removal of Organic Sulfur from Coal by Glacial Acetic Acid–Hydrogen Peroxide Oxidation Process". Environ Prot Chem Ind., 2002, 22(5): 249-253.
[10]. Levent, M., Kaya, Ö., Kocakerim, M., Yiğit, V., Küçük, Ö., "Optimization of Desulphurization of Artvin-Yusufeli Lignite with Acidic Hydrogen Peroxide Solutions", Fuel, 2007, 86: 983-992,
[11]. Gürü, M., Sarıöz, B.V., Çakanyıldırım, Ç., "Oxidative Desulfurization of Tufanbeyli Coal by Hydrogen Peroxide Solution", Energy Sources Part A, 2008, 30:981-987.
[12]. Van Aelst, J., Rodriguez, R.A., Yperman, J., Jul, C.C., Franco, D.V., Mullens, J., and Van Poucke, L.C., "A.p.-t.p.r. Investigation of the Effect of Nitric Acid Leaching on the Sulphur Distribution in Coal", Fuel, 2000, 79: 537-544.
[13]. Karaca, S., Akyürek, M.., Bayrakçeken, S., "The Removal of Pyritic Sulfur from Askale Lignite in Aqueous Suspention by Nitric Acid". Fuel Processing Technology, 2003, 80: 1-8.
[14]. Alvarez, R., Clemente, C., Limon, D.G., "The İnfluence of Nitric Acid Oxidation of Low Rank Coal And Its Impact on Coal Structure". Fuel, 2003, 82: 2007-2015.
[15]. Pietrzak, R., Wachowska, H., "The Influence of Oxidation with HNO3 on the Surface Composition of High-Sulphur Coald: XPS Study". Fuel Processing Technology, 2006, 87: 1021-1029.
[16]. Gürü, M., "Oxidative Desulfurization of Askale Coal by Nitric Acid Solution". Energy Sources Part A, 2007, 29:463-469.
[17]. Alam, H.,G., Moghaddam, A.,Z, Omidkhah, M.,R., "The İnfluence of Process Parameters on Desulfuruzation of Mezino Caol by HNO_3/HCl Leaching", Fuel Processing Technology, 2008, 90: 1-7.
[18]. Rodriguez, R.A., Clemente, C., "Effect of Nitric Acid Attack on the Organic Sulphur Content of Coals", Coal Science, 1995, 1717-1720.
[19]. Sonmez O., Giray E.S., "The influence of process parameters on desulfurization of two Turkis lignites by selective oxidation", Fuel Process Technology, 2001;70: 159–69.
[20]. Gürü, M., Tüzün, F.N., Murathan, A.S., Asan, A., Kıyak, T., "Oxidative Desulfurization of Çayırhan Lignites by Permanganate Solution", Energy Sources Part A, 2008, 30:1508-1515.

[21]. Lee, S., Kesavan, S.K., Ghosh, A., Fullerton, K.L., "Selective Precombustion Desulphurization of Ohio Coals Using Supercritical Fluids", Fuel, 1989, 68:1210-1213.
[22]. Meffe, S., Perkson, A., Trass, O., "Coal Beneficiation and Organic Sulfur Removal", Fuel, 1996, 75:25-30.
[23]. Mukherjee, S., Borthakur, P.C., "Demineralization of Subbitumious High Sulphur Coal Using Mineral Acids" Fuel Processing Technology, 2003, 85:157-164.
[24]. Elsamak, G., G., Öztas, N., A., Yürüm, Y., "Chemical Desulfurization of Turkish Çayırhan lignite with HI Using Microwave and Thermal Energy", Fuel, 2003, 82: 531-537.
[25]. Li, W., Guo, S., "Supercritical Desulphurization of High Rank Coal with Alchol/Water and Alchol/KOH", Fuel Processing Technology, 1996, 46:143-155.
[26]. Lolja, S.A., "A Model for Alkaline Removal of Sulfur from a Low-Rank Coal. Fuel Processing Technology, 1999, 60: 185-194.
[27]. Sugawara, K., Abe, K., Sugawara, T., "Organic Sulfur Removal from Coal by Rapid Pyrolysis with Alkali Leaching and Density Separation", Coal Science, 1995, 1709-1712.
[28]. Ratanakandilok, S., Ngamprasertsith, S., Prasassarakick, P., "Coal Desulphurization with Methanol/Water and Methanol/KOH", Fuel, 2001, 80: 1937-1942.
[29]. Charutawai, K., Ngamprasertsith, S., Prasassarakich, P., "Supercritical Desulphurization of Low Rank Coal with Ethanol/KOH", Fuel Processing Technology, 2003, 84:207-216.
[30]. Mukherjee, S., Borthakur, P.C., "Effect Of Leaching High Sulphur Subbituminous Coal by Potassium Hydroxide and Acid on Removal of Mineral Matter and Sulphur", Fuel, 2003, 82:783-788.
[31]. Mukherjee, S., Borthakur, P.C., "Effect of Alkali Treatment on Ash and Sulphur Removal from Assm Coal", Fuel Processing Technology, 2003, 85:93-101.
[32]. Mukherjee, S., Mahjuddin, S., Borthakur, P.C., "Demineralization and Desulfurization of Subbituminous Soal with Hydrogen Peroxide", Energy&Fuels, 2001, 15:1418-1424.
[33]. Lui, K., Yang, J., Jia, J., Wang, Y., "Desulfurization of Coal Via Low Temperature Atmospheric Alkaline Oxidation", Chemosphere, 2008, 71:183-188
[34]. Demirbaş, A., "Desulfurization of Organic Sulfur From Lignite by An Eletron Transfer Process. Energy Sources Part A", 2006, 28:1295-1301.
[35]. Borah, D., Baruah, M.K., "Electron Transfer Process Part 2. Desulphurization of Organic Sulphur From Feed and Mercury-Treated Coals Oxidized in Air at 50, 100 and 150 °C", Fuel, 2000, 79: 1785-1796.
[36]. Borah, D., Baruah, M.K., Haque, I., "Oxidation of High Sulphur Coal. Part 1. Desulphurization and Evidance of the Formation of Oxidised Organic Sulphur Species", Fuel, 2001, 80:501-507.
[37]. Borah, D, Mrinal K, Baruahb T, Haquea I., "Oxidation of high sulphur coal. 3. Desulphurisation of organic sulphur by peroxyacetic acid (produced in situ) in presence of metal ions", Fuel Process Technology, 2005, 86:959–76
[38]. Jorjani, E., Rezai, B., Vossouhgi, M., and Osanloo, M., "Desulfurization of Tabas Coal with Microwave Irridation/Peroxyacetic Acid Washing at 25, 55 and 85 ^{o}C", Fuel, 2004, 83: 943-949.
[39]. Zhao, H., Li, Y., Qu, Y., Duan, Z., Zhang J., and Liu J., "Experimental Study on Microwave Desulfurization of Coal", International Conference on Materials for Renewable Energy& Environment, 2011, 1706-1710.
[40]. International Standard, ISO 334. Solid mineral fuels – determination of total sulfur-Eschka method; 1992. p. 1–5.
[41]. International Standard, ISO157. Coal – DEtermination of forms of sulfur; 1992. p. 1–15.