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Optimization of some parameters on desulfurization process of Muğla Yatağan Bağyaka lignite by ultrasonic waves

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Research Article

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ABSTRACT

In this study, the desulfurization process developed using ultrasonic waves for Muğla Yatağan Bağyaka lignite had the optimum conditions for parameters affecting the ash and sulfur removal potentials determined with the Surface Response Method and a model created. The process parameters to obtain optimum desulfurization and ash removal were chosen as the ultrasonic treatment time, solid content, concentration of chemical reactive (H_2O_2) and reactive volume, and the optimum values were determined. Using this data with the aid of the Design Export 7.0 program, the regression model was found as a second degree polynomial equation. The coefficients of determination (R^2) for desulfurization and ash removal regressions were 0.96 and 0.97, respectively, in the determined model. The model prediction values and experimental results for desulfurization and ash removal in the investigated parameter intervals were compared and the fit was identified. In the experimental removal of sulfur types with optimum desulfurization it was found that pyritic 17.02%, sulfate 16.67% and organic 9.52%.

1. Introduction

Physical methods are commonly used in coal cleaning facilities to remove the ash content. Though physical methods remove coal ash to a significant degree, the sulfur content remains (Aksoy et al., 1981; Akalın and Öz, 1989; Atak and Güney, 1989; Tosun et al., 1994; Özbayoğlu and Mamurekli, 2002; Tuncalı et al., 2002). To remove a significant portion of sulfur in the chemical-based coal desulfurization process, longer treatment time and the use of solvents increases costs and difficulties are encountered in neutralising coal at the end of the process (Mukherjee and Borthaku, 2003; Nabeel et al., 2009; Tosun, 2012). Biological methods remove pyritic sulfur up to 70-80% in coal via consumption by special bacteria; however, removal of organic sulfur is very low and difficult (Göktepe, 2002). Biological methods can be applied to very finely ground coal and require times lasting days, and also require significant security precautions to protect the biological environment and prevent environmental effects (Tosun et al., 1994; Tosun, 2012).

Using new generation technologies like ultrasonic waves in the sulfur removal increases the process efficiency of physical coal cleaning processes and/or ensure equipment savings (Angle et al., 1988; Buttermore and Slomka, 1991; Ambedkar et al., 2011*a*, 2011*b*; Şahinoğlu and Uslu, 2013). When ultrasonic waves are used in the chemical demineralization and desulfurization processes, they are stated to increase process efficiency (Baruah and Khare, 2007; Ambedkar et al., 2011*a*, 2011*b*; Saikia et al., 2014*a*, 2014*b*, 2016). When conventional methods (using HNO_3 and H_2O_2 as reactives, in the order of wetting; 300 min and mixing; 500, 1000 rpm, 60 min) for coal desulfurization are compared with ultrasonic processes (with 20 kHz frequency prop; with reactives (HNO_3, 23 min and H_2O_2, 30 min) and aqueous), total sulfur removal with ultrasonic methods (with 20 kHz frequency; with reactives 87% (HNO_3), 74%

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(H_2O_2) and aqueous 55%) is higher compared to conventional methods [with wetting, 46% (HNO_3) and 35% (H_2O_2); mixing rates of 500 and 1000 rpm, 25% (HNO_3), 29% (H_2O_2) and 24% (HNO_3), 27 (H_2O_2%), respectively] and when reactives are used, this removal conspicuously increases (Ambedkar et al., 2011*b*). After HF/HNO_3 acid leach processes Iranian coal with sulfur content of 1.89% reached a sulfur content of 1.26% (sulfur removal 33.33%), while after pretreatment with ultrasonic waves and then the leach process sulfur content was found to fall to 1.16% (sulfur removal 38.62%) (Royaei et al., 2012).

When ultrasonic waves are applied to a mixture of coal and water, the physical bonds between coal and mineral material are broken and with the mass transfer mechanism two possible events occur as mineral material is more easily dissolved and removed. In environments with ultrasonic waves, oxidation occurs called the advanced oxidation process and this transforms the sulfur in coal into water-soluble sulfate (Özkan, 1998; Gül, 2001; Ambedkar et al. 2011*a*, 2011*b*; Royaei et al., 2012; Saikia et al., 2014*a*, 2014*b*, 2016). During effective desulfurization, strong oxidant like environment friendly H_2O_2 is aided by the ultrasonic system ensure sulfur removal in a short time interval. When hydrogen peroxide reacts with almost all forms of sulfur and converts them into soluble sulfate it does not produce any harmful by-products (Saikia et al., 2016). The desulfurization process with ultrasonic waves is a method ensuring removal with minimum treatment time and less use of solvents and is recommended for its capabilities at industrial scales (Ambedkar et al., 2011*b*; Saikia et al., 2014*a*, 2014*b*).

Modelling and optimization of chemical processes carry great importance in terms of economic and technically efficient operation of these processes. Response Surface Method (RSM) is a statistical tool that has been used for optimization of ash and sulfur removal with a variety of methods in recent years and in assessing the single and binary/multiple effects of process parameters. The most commonly applied form of the response surface method is Central Composite Design (CCD) created with second degree equations (Karacan et al., 2007; Montgomery, 2009; Türk, 2016).

In this study, Muğla Yatağan (MY) Bağyaka lignite was used with total sulfur content of 2.69% and organic sulfur responsible for a large proportion of 2.10% of this sulfur. MY Bağyaka lignite was determined to have washability of moderately difficult degree (65% recovery, 20% ash removal and no sulfur removal, Akalın and Öz, 1989) or very difficult degree (18.84% ash removal and no sulfur removal, Tuncalı et al., 2002); as a result the necessity to reduce the high sulfur amounts unable to be removed with washing was stated. In this way, this research and development (R&D) study of the chemical desulfurization process conducted using ultrasonic waves for MY Bağyaka lignite to determine the optimum conditions for parameters affecting the ash and sulfur removal potentials with the response surface method and a model was developed. With this aim, the process parameters to obtain optimum desulfurization (sulfur removal) and ash removal of ultrasonic treatment time, solid content, chemical reactive (H_2O_2) concentration and reactive (H_2O_2) volume were chosen and optimum values were determined.

2. Material and Method

2.1. Material

The MY Bağyaka lignite used in our study was obtained by blending samples stacked at the entrance to Yatağan Thermal Power Plant. Lignite samples were reduced to -250 µm particle size after crushing, milling and screening processes, and after that were placed in airtight bags for use in experiments. The chemical analysis results of the lignite were determined in accordance with ASTM standards (D7582, D4239, D5865), and sulfur analysis types were determined according to TS 329 ISO 157 (Table 1). The particle size distribution of lignite was determined using a Malvern Mastersizer 2000 (Hydro 2000 MU) particle size analyser (Table 2).

2.2. Experimental Procedure

According to the design matrix shown in table 3, 30 experiments were performed with the parameters of ultrasonic treatment time (5, 10, 20, 30, 35 min), solid content (5, 10, 20, 30, 35%), concentration of chemical reactive (0, 0.5, 1.5, 2.5, 3 M 30% H_2O_2) and chemical reactive volume (20, 40, 80, 120, 140 ml H_2O_2). Keeping the total volume as 200 ml for all the experiment, the lignite (-250 µm) and a homogeneous mixture of distilled water and hydrogen peroxide (30%) were placed in a 500 ml erlenmeyer flask and they were processed in an ultrasonic bath with power of 500 W and frequency of 28 kHz for the desired treatment time. The lignite mixture obtained at the end of the experiment was filtered with rough filter paper and washed with hot distilled water. The

Table 1- Chemical analysis of Muğla Yatağan Bağyaka lignite.

	Air dried (ad)	**Dry basis (db)**	**Dry ash free (daf)**
Proximate Analysis			
Moisture (%)	8.39	–	–
Ash (%)	35.97	39.27	–
Volatile matter (%)	39.45	43.06	70.90
Fixed Carbon (%)	16.19	17.67	29.10
Sulfur Analysis			
Total sulfur (%)	2.47	2.69	–
Pyritic sulfur (%)	0.43	0.47	–
Sulfate sulfur (%)	0.11	0.12	–
Organic sulfur (%)	1.93	2.10	–
Lower calorific analysis			
Lower calorific value (kcal/kg)	3069	3404	5604

Table 2- Particle size distribution for Muğla Yatağan Bağyaka lignite.

Lignite	d(0,1), µm	d(0,5), µm	d(0,9), µm	d(sauter), µm	SSA[a], m^2/g
MY Bağyaka	2.718	17.399	120.798	6.494	0.924

d(0,1), d(0,5), d(0,9): particle diameters at 10%, 50%, 90% points, d(sauter): Sauter mean diameter, a: Specific surface area.

Table 3- Independent process parameters and coding levels.

Parametre	Code	Unit	Coded Parameter Levels				
			-α	-1	0	+1	+α
Time	X_1	min	5	10	20	30	35
Solid content	X_2	%	5	10	20	30	35
Reactive concentration	X_3	M	0	0.5	1.5	2.5	3
Reactive volume	X_4	ml	20	40	80	120	140

washed lignite remaining on the filter paper was dried overnight in an oven at 80±5ºC. The obtained lignite samples had ash and total sulfur contents identified. The flow schematic of the process is given in figure 1.

Desulfurization (sulfur removal, DE), Ash Removal (AR) and Recovery (R) were determined based on the following equations (1), (2) and (3), respectively. In these equations, C_F and C_P are the

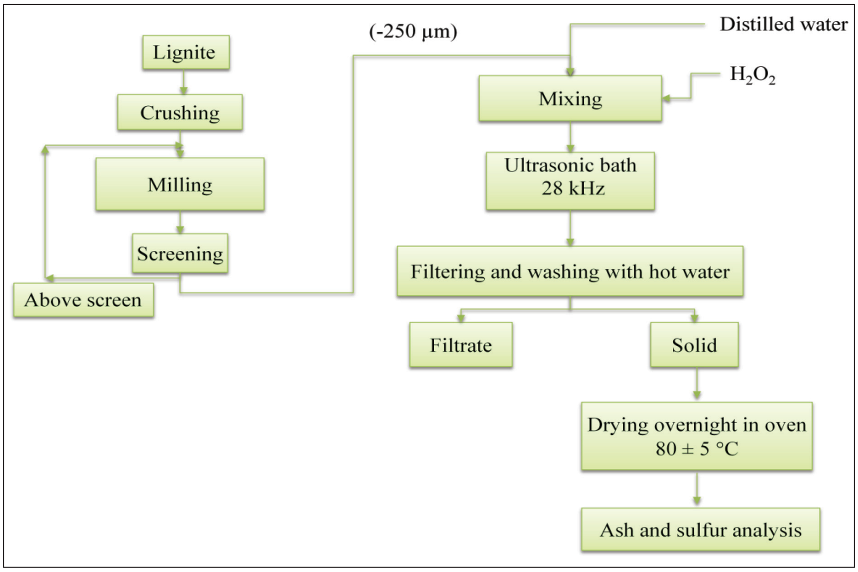


Figure 1- Flow chart of desulfurization and ash removal process for lignite with ultrasonic waves.

total % sulfur content in original feed and ultrasonic processed lignite; A_F and A_P are the % ash content in original feed and ultrasonic processed lignite; and C_a and C_f are the ash-free (g) amounts of ultrasonic processed and original feed lignite.

$$DE\,(\%) = [(C_F - C_P)/C_F]x100 \quad (1)$$

$$AR\,(\%) = [(A_F - A_P)/A_F]x100 \quad (2)$$

$$R\,(\%) = (C_a\,/\,C_f)x100 \quad (3)$$

2.3. Experimental Design

The response surface method (RSM) is defined as a method using mathematical and statistical techniques to develop a sufficient functional relationship between the response and independent variables. Within the experimental planning, preliminary experiments for factors affecting the process are performed, and levels are explored. After the levels are determined, the experimental studies in the pattern predicted by the program are completed and assessed with the aid of the program to reveal the optimum conditions of the process (Aygün, 2012). Generally to represent the system, second degree equations given in Equation (4) are used.

$$Y = \beta_0 + \Sigma\beta_i X_i + \Sigma\, \beta_{ii} X_i^2 + \Sigma\, \beta_{ij} X_i X_j \quad (4)$$

Here Y: predicted response, β_{ii}: square coefficient, β_i: linear coefficient, β_0: model constant, βij: coefficient showing mutual interaction between parameters, and Xi and Xj: independent variables of the process. Regression analysis with the second degree polynomial equation in the model estimates the coefficients to create the regression equation. With the aid of the created equation predicted results are obtained for the response and the accuracy of the predictions are checked to see if the model is sufficient or not.

The most commonly applied form of RSM is Central Composite Design (CCD) with a second degree response surface model created. The method has two factorial points. These are axis points (α) and central points. With k factor numbers (number of independent variables) and n_0 central point, the total number of design points is $N = 2^k + 2k + n_0$. Here the factor levels are coded as -1 for minimum and +1 for maximum. Axis points are beyond the two level points determined by the designer and are +α and –α values determined by the program. The central points are repeated points to estimate the experimental error. Finally in CCD each parameter has five levels. These are the factor points represented by +1 and -1, axis points represented by +α and –α and the central point represented by 0 (Montgomery, 2009; Türk, 2016).

In this study the independent variables of the system, their mutual interactions, and effects on obtaining the product were statistically analysed, modelled with RSM and had experiments designed with CCD. To determine optimum desulfurization (Y_1) and ash removal (Y_2) conditions, with the CCD method of RSM $2^4 + 2\,(4) + 6 = 30$ experiments were planned for 4 parameters. While 24 experiments were normal experiments, 6 were repeated experiments at the central points of individual variables. The parameters used in the experimental design were determined as ultrasonic treatment time (X_1), solid content (X_2), chemical reactive concentration (30% H_2O_2) (X_3) and reactive volume (H_2O_2) (X_4). The minimum, maximum, axis and central point values for variables given in table 3 form the experimental design matrix. Using this data with the aid of the Design Export 7.0 program, statistical analysis was performed and a regression model obtained.

3. Results and Discussions

According to the 30 experiments in the design matrix given in table 3 for treatment time (min), solid content (%), reactive concentration (M) and reactive volume (ml) parameters, the experimental (observed) data for desulfurization (DE) and ash removal (AR) of MY Bağyaka lignite are shown in table 4. With the aid of Design Export 7.0 program using this experimental data, statistical analysis was performed and a regression model obtained. The regression models of the desulfurization (Y_1) and ash removal (Y_2) are in the form of second degree polynomial equations given in Equations (5) and (6).

- Desulfurization

$$Y_1 = 6.60 - 0.40X_1 - 0.34X_2 + 1.02X_3 + X_4 - 0.094X_1X_2 + 0.23X_1X_3 + 0.37X_1X_4 + 0.32X_2X_3 - 0.84X_2X_4 + 0.046X_3X_4 - 0.40X_1^2 - 0.53X_2^2 - 0.28X_3^2 + 0.13X_4^2 \quad (5)$$

- Ash removal

$$Y_2 = 2.57 - 0.42X_1 - 0.79X_2 + 0.15X_3 + 0.13X_4 + 0.044X_1X_2 + 0.027X_1X_3 - 0.29X_1X_4 - 0.25X_2X_3 - 0.18X_2X_4 + 0.16X_3X_4 + 0.37X_1^2 + 0.24X_2^2 - 0.72X_3^2 - 0.13X_4^2 \quad (6)$$

Table 4- Experimental design matrix, desulfurization and ash removal results for MY Bağyaka lignite.

Run	Coded level of parameters				Experimental parameters				Observed values	
	X_1	X_2	X_3	X_4	X_1, min	X_2, %	X_3, M	X_4, ml	DE, %	AR, %
1	0	0	0	0	20	20	1.5	80	7.06	2.65
2	+1	+1	-1	-1	30	30	0.5	40	3.35	1.71
3	-1	-1	+1	+1	10	10	2.5	120	6.32	5.09
4	0	0	0	+α	20	20	1.5	140	9.29	1.43
5	0	0	0	0	20	20	1.5	80	5.95	2.24
6	-1	+1	-1	+1	10	30	0.5	120	3.35	2.55
7	-1	+1	+1	+1	10	30	2.5	120	5.95	2.52
8	+1	-1	+1	-1	30	10	2.5	40	4.09	2.83
9	+1	+1	+1	+1	30	30	2.5	120	7.06	1.15
10	-1	-1	-1	+1	10	10	0.5	120	6.32	3.13
11	0	-α	0	0	20	5	1.5	80	6.32	5.37
12	+1	-1	-1	+1	30	10	0.5	120	5.95	2.11
13	0	0	0	0	20	20	1.5	80	7.06	2.62
14	0	0	0	0	20	20	1.5	80	6.69	2.57
15	0	0	0	0	20	20	1.5	80	6.32	2.34
16	0	0	0	0	20	20	1.5	80	6.69	2.60
17	+1	-1	+1	+1	30	10	2.5	120	11.15	3.44
18	0	+α	0	0	20	35	1.5	80	4.09	1.27
19	+1	+1	+1	-1	30	30	2.5	40	7.81	1.25
20	-1	+1	+1	-1	10	30	2.5	40	6.69	1.73
21	-1	+1	-1	-1	10	30	0.5	40	3.72	1.20
22	-1	-1	+1	-1	10	10	2.5	40	5.20	2.24
23	0	0	+α	0	20	20	3.0	80	6.32	0.81
24	0	0	-α	0	20	20	0.0	80	5.20	1.53
25	+α	0	0	0	35	20	1.5	80	5.58	2.70
26	-1	-1	-1	-1	10	10	0.5	40	2.97	2.88
27	+1	-1	-1	-1	30	10	0.5	40	4.46	1.48
28	-α	0	0	0	5	20	1.5	80	5.20	4.99
29	+1	+1	-1	+1	30	30	0.5	120	4.83	1.12
30	0	0	0	-α	20	20	1.5	20	4.09	3.54

DE: Desulfurization, AR: Ash removal.

The coefficients of determination (R^2) for desulfurization and ash removal were determined as 0.96 and 0.97, respectively. The results of analysis of variance (ANOVA) to determine the significance of the model and the significance of terms in the model are given in tables 5 and 6.

High F value indicates the significance of the relevant term. Whether the F value has sufficiently high value or not is assessed with the p value. While low p values indicate rejection of the hypothesis, at the same time they represent the significance of the variable (whether the parameter has a greater effect on the result) (Aslan and Ünal, 2009; Kumar et al., 2009; Amani-Ghadima et al., 2013; Sabuncu, 2014). If the p value is smaller than 0.05 it is significant, if it is larger than 0.1 it is insignificant. In this situation the significant model terms are X_3, X_4 and X_2X_4 (Table 5) for desulfurization; and X_1, X_2, and X_3^2 (Table 6) for ash removal. The observed values for desulfurization, ash removal and the predicted values obtained in the model using Equations (5) and (6) are given together in table 7.

3.1. Optimization of Process Parameters

The desulfurization and ash removal results for MY Bağyaka lignite under optimum conditions found with the numerical optimization method for desulfurization (ODE), ash removal (OAR) and recovery are given in table 8. For desulfurization from MY Bağyaka lignite, the optimum process parameters found with the numerical optimization method were time 30 min, solid content 10%, chemical reactive concentration 2.5 M and reactive volume 120 ml producing 95.87% recovery and 9.54% optimum desulfurization. At this optimum desulfurization, the model prediction value for ash removal was 3.25%.

Table 5- Analysis of variance (ANOVA) for desulfurization of MY Bağyaka lignite.

Source	Total of squares	df	Mean of squares	F value	p value
Model	71.00	14	5.07	3.93	0.0063 significant
X_1-Time	3.45	1	3.45	2.67	0.1229
X_2-Solid content	2.42	1	2.42	1.88	0.1908
X_3-Reactive concentration	21.51	1	21.51	16.68	0.0010
X_4-Reactive volume	20.38	1	20.38	15.80	0.0012
X_1X_2	0.14	1	0.14	0.11	0.7458
X_1X_3	0.86	1	0.86	0.67	0.4256
X_1X_4	2.19	1	2.19	1.70	0.2121
X_2X_3	1.69	1	1.69	1.31	0.2703
X_2X_4	11.22	1	11.22	8.70	0.0099
X_3X_4	0.034	1	0.034	0.027	0.8728
X_1^2	1.81	1	1.81	1.40	0.2551
X_2^2	3.24	1	3.24	2.51	0.1340
X_3^2	0.93	1	0.93	0.72	0.4093
X_4^2	0.19	1	0.19	0.15	0.7067
Residual	19.34	15	1.29		
Lack of fit	18.52	11	1.68	8.20	0.0283
Pure Error	0.82	4	0.21		
Total	90.34	29			

Table 6- Analysis of variance (ANOVA) for ash removal of MY Bağyaka lignite.

Source	Total of Squares	df	Mean of square	F value	p value
Model	28.72	14	2.05	2.79	0.0288 significant
X_1-Time	3.81	1	3.81	5.19	0.0378
X_2-Solid content	12.68	1	12.68	17.26	0.0008
X_3-Reactive concentration	0.44	1	0.44	0.59	0.4529
X_4-Reactive volume	0.34	1	0.34	0.46	0.5090
X_1X_2	0.032	1	0.032	0.043	0.8387
X_1X_3	0.012	1	0.012	0.016	0.9018
X_1X_4	1.37	1	1.37	1.87	0.1914
X_2X_3	0.97	1	0.97	1.31	0.2696
X_2X_4	0.52	1	0.52	0.71	0.4124
X_3X_4	0.39	1	0.39	0.54	0.4753
X_1^2	1.58	1	1.58	2.15	0.1631
X_2^2	0.66	1	0.66	0.90	0.3575
X_3^2	5.87	1	5.87	7.99	0.0128
X_4^2	0.20	1	0.20	0.27	0.6128
Residual	11.02	15	0.73		
Lack of fit	10.90	11	0.99	35.11	0.0018
Pure Error	0.11	4	0.028		
Total	39.74	29			

Table 7- Observed and predicted results for desulfurization and ash removal for MY Bağyaka lignite.

Run	Experimental parameters				DE, %		AR, %	
	X_1, min	X_2, %	X_3, M	X_4, ml	Observed	Predicted	Observed	Predicted
1	20	20	1.5	80	7.06	6.60	2.65	2.57
2	30	30	0.5	40	3.35	3.42	1.71	1.75
3	10	10	2.5	120	6.32	7.34	5.09	4.71
4	20	20	1.5	140	9.29	8.39	1.43	2.47
5	20	20	1.5	80	5.95	6.60	2.24	2.57
6	10	30	0.5	120	3.35	3.50	2.55	2.14
7	10	30	2.5	120	5.95	5.82	2.52	2.20
8	30	10	2.5	40	4.09	5.04	2.83	2.90
9	30	30	2.5	120	7.06	7.64	1.15	0.91
10	10	10	0.5	120	6.32	6.32	3.13	3.67
11	20	5	1.5	80	6.32	5.92	5.37	4.29
12	30	10	0.5	120	5.95	7.58	2.11	2.10
13	20	20	1.5	80	7.06	6.60	2.62	2.57
14	20	20	1.5	80	6.69	6.60	2.57	2.57
15	20	20	1.5	80	6.32	5.80	2.34	3.36
16	20	20	1.5	80	6.69	6.60	2.60	2.57
17	30	10	2.5	120	11.15	9.54	3.44	3.25
18	20	35	1.5	80	4.09	4.89	1.27	1.93
19	30	30	2.5	40	7.81	6.49	1.25	1.29
20	10	30	2.5	40	6.69	6.15	1.73	1.40
21	10	30	0.5	40	3.72	4.01	1.20	1.97
22	10	10	2.5	40	5.20	4.32	2.24	3.20
23	20	20	3.0	80	6.32	7.50	0.81	1.18
24	20	20	0.0	80	5.20	4.43	1.53	0.74
25	35	20	1.5	80	5.58	6.31	2.70	2.77
26	10	10	0.5	40	2.97	3.48	2.88	2.78
27	30	10	0.5	40	4.46	3.27	1.48	2.38
28	5	20	1.5	80	5.20	5.11	4.99	4.04
29	30	30	0.5	120	4.83	4.38	1.12	0.74
30	20	20	1.5	20	4.09	5.40	3.54	2.08

DE: Desulfurization, AR: Ash removal.

Table 8- Desulfurization, ash removal and recovery results under optimum conditions found with the numerical optimization method for MY Bağyaka lignite.

	Experimental parameters				Lignite (daf), g		Product (db), %		Removal, %				R, %
					Feed	Product	Sulfur	Ash	Sulfur		Ash		
	X_1	X_2	X_3	X_4					O	P	O	P	
ODE	30	10	2.5	120	11.13	10.67	2.39	37.92	11.15	9.54	3.44	3.25	95.87
OAR	10	10	2.5	120	11.13	10.65	2.52	37.27	6.32	7.34	5.09	4.71	95.69

ODE: Optimum values for lignite desulfurization conditions, OAR: Optimum values for lignite ash removal conditions, R: Recovery, X_1: Time, X_2: Solid content, X_3: Reactive concentration (H_2O_2), X_4: Reactive volume (H_2O_2), O: Observed, P: Predicted, db: dry basis, daf: dry ash free.

For ash removal from MY Bağyaka lignite, the optimum process parameters found with the numerical optimization method were time 10 min, solid content 10%, chemical reactive concentration 2.5 M and reactive volume 120 ml producing 95.69% recovery and 4.71% optimum ash removal. At this optimum ash removal, the model prediction value for desulfurization was 7.34%. The optimum desulfurization and ash removal of MY Bağyaka lignite of the observed results were 11.15% and 5.09%, respectively. According to optimization results to confirm the accuracy of the process, repeated experimental results were 10.29% and 4.94%, respectively. For desulfurization and ash removal of MY Bağyaka lignite, according to optimization results to confirm the accuracy of the process, repeated experimental results were 10.29%

and 4.94%, respectively. From the obtained results, the model in the form of second degree polynomial equation may be said to have accuracy and validity proven for desulfurization and ash removal.

In experiments performed according to the design matrix in table 3, other parameters were fixed (solid content 20%, chemical reactive concentration (H_2O_2) 1.5 M and reactive volume (H_2O_2) 80 ml) and ultrasonic process time was increased from 5 min to 20 min, which increased sulfur removal from 5.20 % to 7.06% while ash removal fell from 4.99% to 2.65%. When pure water is used as reactive instead of hydrogen peroxide, the other parameters were fixed (time 20 min, solid content 20%, chemical reactive concentration (water) 0.0 M and reactive volume (water) 80 ml), and after ultrasonic wave treatment sulfur removal was 5.20% and ash removal was 1.53%. When pure water is used instead of hydrogen peroxide, sulfur removal fell from 7.06% to 5.20% while ash removal fell from 2.65% to 1.53%. The use of hydrogen peroxide as reactive increased sulfur and ash removal. In the hydrogen peroxide environment, oxidation occurs with the ultrasonic waves and this transforms the sulfur present in the coal into water-soluble sulfate (Ambedkar et al. 2011*a*, 2011*b*; Saikia et al., 2014*a*, 2014*b*, 2016). For effective desulfurization strong oxidants, like cost efficient and environmentally-friendly hydrogen peroxide, with the aid of an ultrasonic system produce sulfur removal in a short time interval.

For desulfurization and ash removal from MY Bağyaka lignite, the Malvern particle size analyser results for original and optimum conditions are given in table 9. As seen in the table 9, the specific surface area values (m^2/g) of lignite fell from 0.924 to 0.631 for desulfurization and from 0.924 to 0.818 for ash removal. This reduction is greater for desulfurization compared to ash removal. During desulfurization of lignite with ultrasonic waves, the pore volume of the lignite is reduced and as a result the specific surface area reduced. When the desulfurization parameters are fixed (solid content 10%, chemical reactive concentration (H_2O_2) 2.5 M and reactive volume (H_2O_2) 120 ml), increasing the time from 10 min to 30 min increases sulfur removal from 6.32% to 11.15% while ash removal falls from 5.09% to 3.44%. This reduction in ash removal may be due to fine minerals being held in the interior sections of the lignite or in large pores on the surface during the reaction.

Additionally during the desulfurization of MY Bağyaka, observed analysis types of lignite under original and optimum conditions, sulfur analysis types, removal of ash and sulfur analysis types are given in table 10 as dry basis. In table 10, it appears the organic sulfur amount in original lignite is higher compared to pyritic and sulfate sulfur. During combustion of lignite, a large portion of organic sulfur transforms to sulfur dioxide (SO_2) (Ateşok, 1986; Şahinoğlu, 2006). As organic sulfur is bound to the molecular structure of lignite, as long as chemical bonds holding the molecules together are not broken, it is not possible to remove it from lignite (Özbayoğlu, 1982). With desulfurization of MY Bağyaka lignite, total, pyritic, sulfate and organic sulfur reduced. Total sulfur fell from 2.69% to 2.39%, pyritic sulfur fell from 0.47% to 0.39%, sulfate sulfur fell from 0.12% to 0.10% and organic sulfur fell from 2.10% to 1.90%. It appeared

Table 9- Malvern particle size analysis result under original and optimum conditions for desulfurization and ash removal of MY Bağyaka lignite.

Lignite	d(0,1), µm	d(0,5), µm	d(0,9), µm	d(sauter) µm	SSA[a], m²/g
Original	2.718	17.399	120.798	6.494	0.924
Optimum desulfurization	4.127	36.742	242.809	9.502	0.631
Optimum ash removal	3.170	20.447	144.227	7.335	0.818

d(0,1), d(0,5), d(0,9): particle diameters at 10%, 50%, 90% points, d(sauter): Sauter mean diameter, a: Specific surface area.

Table 10- Sulfur analysis types and removal of sulfur analysis types (observed) under original and optimum conditions for desulfurization of MY Bağyaka lignite (dry basis).

MY Bağyaka Lignite	Sulfur, %					Sulfur removal, %				Ash removal, %
	Pyritic	Sulfate	Organic	Total		Pyritic	Sulfate	Organic	Total	
Original	0.47	0.12	2.10	2.69		-	-	-	-	-
Optimum condition	0.39	0.10	1.90	2.39		17.02	16.67	9.52	11.15	3.44

that ultrasonic waves (28 kHz) in the hydrogen peroxide environment had a positive effect on removal of sulfur types from lignite.

Saika et al. (2014*a*) used 20 kHz frequency prop with ultrasonic treatment time of 180 min and H_2O_2 reactive on four different Indian coals (with low ash, high sulfur content and high organic sulfur content, with similar rank and origin obtained from different areas) and obtained removal of sulfur analysis types (pyritic 16.66-51.21%, sulfate 32.83-47.61%, organic 4.05-47.60% and total 19.81-31.09%) and ash removal (7.78-32.47%). In this study similar to the literature, desulfurization of MY Bağyaka lignite in a short time of 30 min obtained total sulfur removal of 11.15%, pyritic sulfur removal of 17.02%, sulfate sulfur removal of 16.67%, organic sulfur removal of 9.52% and ash removal of 3.44%. The differences in sulfur types and ash removal in coals may be due to the nature of mineral material composition and organic sulfur compounds in coal (Grounds and Wandless, 1952; Ely and Barnhart, 1963; Lowry, 1963; Ünal, 1999; Ambedkar et al., 2011*a*, 2011b; Saikia et al., 2014*a*, 2014*b*, 2016).

3.2. Three Dimensional (3D) Surface Figures

In desulfurization and ash removal from MY Bağyaka lignite, 3 dimensional (3D) surface graphics based on the interaction of optimum process parameters obtained using the numerical optimization method in Equations (5) and (6) were obtained. The correlation between the variables and effects are more clearly understood with the aid of these graphics. Though the model included four variables, on each graphic two variables were fixed at the centre and the other two variables had values within the limits. The response surface graphics produced 12 responses as a function of the two fixed variables and the two variables within the limits. When the two variables for desulfurization and ash removal are fixed in the centre, and the other two variables have values within the determined limits, the obtained three dimensional surface graphics are shown in figure 2 (a-f) and figure 3 (a-f).

As seen on figure 2 (a-f), for desulfurization as the ultrasonic treatment time, chemical reactive concentration and reactive volume increase, sulfur removal increased; however as solid content increased sulfur removal reduced. For ash removal, as chemical reactive concentration and reactive volume increased, ash removal increased; as ultrasonic treatment time and solid content increased, ash removal reduced (Figure 3 (a-f)). Within the investigated parameter intervals on 3D surface graphics, it appears all variables play an important role in desulfurization and ash removal from MY Bağyaka lignite.

4. Conclusion

In this study, the sulfur and ash removal potential with ultrasonic waves was investigated for MY Bağyaka lignite.

1. In determination of optimum conditions, experiments were performed for 4 parameters using the central composite design of the response surface method. With this aim, the optimum values were determined for the process parameters of ultrasonic treatment time, solid content, chemical reactive concentration and reactive volume to obtain optimum desulfurization (sulfur removal) and ash removal. With the aid of Design Export 7.0 program using this data, statistical analysis was performed and a regression model was obtained. The desulfurization (Y_1) and ash removal (Y_2) given in the model equations were stated as functions of time (X_1), solid content (X_2), chemical reactive concentration (X_3) and reactive volume (X_4) coded units. The regression model was found to be a second degree polynomial equation. The coefficients of determination for desulfurization and ash removal were determined as 0.96 and 0.97, respectively.

2. With the numerical optimization method for MY Bağyaka lignite with 95% and above recovery, the optimum desulfurization and ash removal prediction values were 9.54% (time 30 min, solid content 10%, chemical reactive concentration 2.5 M and reactive volume 120 ml) and 4.71% (time 10 min, solid content 10%, chemical reactive concentration 2.5 M and reactive volume 120 ml).

3. During desulfurization and ash removal from MY Bağyaka lignite, specific surface area values were reduced. During desulfurization of lignite with ultrasonic waves, the pore volume of the lignite reduced and as a result there was a reduction in specific surface area.

4. In the literature, it was determined to be difficult to remove sulfur with physical separation

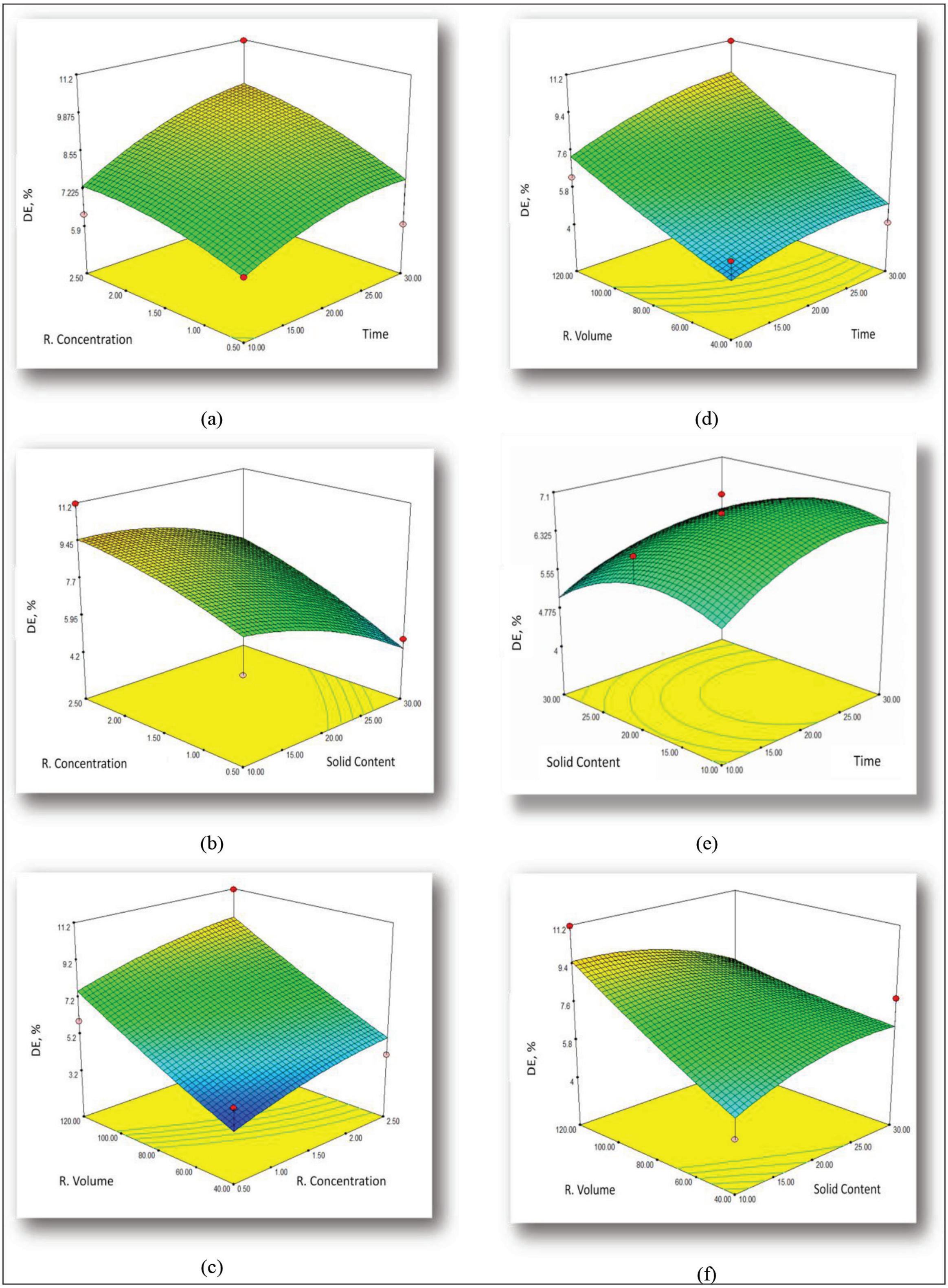
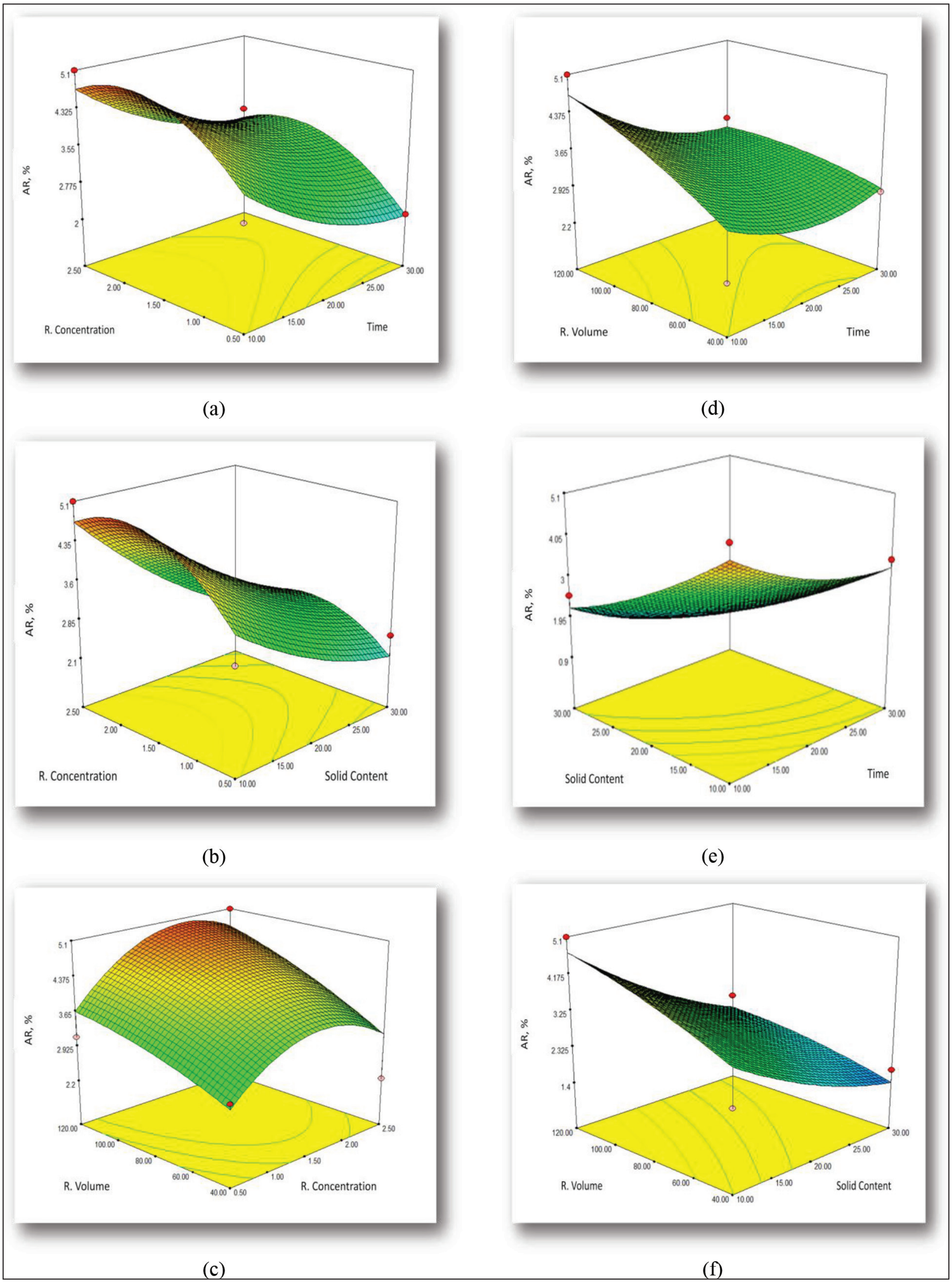


Figure 2- Response surface graphs showing of the effect of two variables on desulfurization (DE) of MY Bağyaka lignite (other two variables are held at center level): (a) reactive concentration and time; (b) reactive concentration and solid content; (c) reactive volume and reactive concentration; (d) reactive volume and time; (e) solid content and time; (f) reactive volume and solid content.



(a) (d)

(b) (e)

(c) (f)

Figure 3- Response surface graphs showing of the effect of two variables on ash removal (AR) from MY Bağyaka lignite desulfurization (other two variables are held at center level): (a) reactive concentration and time; (b) reactive concentration and solid content; (c) reactive volume and reactive concentration; (d) reactive volume and time; (e) solid content and time; (f) reactive volume and solid content.

methods due to the high organic sulfur amounts in MY Bağyaka lignite. The chemical desulfurization process with ultrasonic waves had a positive effect on removal of all sulfur types (pyritic 17.02%, sulfate 16.67% and organic 9.52%) with low treatment time, low solid content, and low chemical reactive concentration and volume.

5. On dry basis, with desulfurization optimization total sulfur content reduced from 2.69 to 2.39%, with ash content reducing from 39.27 to 37.92%; with ash removal optimization, total sulfur content reduced from 2.69 to 2.52%, with ash content reducing from 39.27 to 37.37%.

6. According to optimization results based on repeated results to confirm the accuracy of the process, the model in the form of a second degree polynomial equation was seen to have accuracy and validity confirmed for desulfurization and ash removal within the interval of the investigated parameters.

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