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Feasibility of Using a Mixed Solution of Potassium Tert-Butoxide and Tetrahydrofuran with Ultrasonic-Assisted Process for Desulfurization of High-Sulfur Coal

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The research investigates an effective reductive desulfurization method of high-sulfur coal using a combination of potassium tert-butoxide and tetrahydrofuran (KOtBu/THF), strengthened by ultrasonic waves. This study aims to extract organic sulfur from coal by disrupting the chemical bonds that bind sulfur to the coal's macromolecular structure with ultrasonic waves, facilitating its separation with the influence of concentration, time, and temperature. Fourier transform infrared spectroscopy (FTIR) investigation indicated a decrease in the relative abundance of aliphatic sulfur compounds, including thiol, thiophene, and sulfone, as well as the organic matter of the treated coal. Optimal conditions, including concentration, temperature, and processing time, were identified using the Central Composite Design-Response Surface Methodology (CCD-RSM). This method improves the inefficiencies and imprecision of traditional techniques. A maximum decrease of 66.76% of organic sulfur removal was achieved by sonicating the coal at 70 °C for 30 minutes with a 25% w/v solution of KOtBu/THF. The chemical effects were assessed by measuring hydroxyl radical production under ultrasonic conditions using the iodine release method. The experimental results indicated a correlation between hydroxyl radical production and the degree of desulfurization. Afterward, the formation of low molecular weight fragments from aliphatic carbons resulted in enhanced mass loss during thermogravimetric analysis (TGA). These findings confirm that the synergistic physical and chemical effects of ultrasound are crucial to the desulfurization process, offering a foundation for further optimization of coal desulfurization techniques.

Keywords: Coal desulfurization; potassium tert-butoxide; sulfur; ultrasonics; response surface methodology

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Coal remains a prominent fossil fuel, playing an important role for the next few decades [1]. However, direct combustion of high-sulfur coal results in the production of hydrogen sulfide and sulfur dioxide [2], which are released as gases and have a substantial impact on air pollution and the creation of acid rain [3]. Sulfur's presence presents hazards to agricultural goods, contributes to the loss of the ozone layer, induces metal corrosion, and damages ecological systems [4]. However, high-quality coal reserves are gradually depleting, and many high-sulfur coal reserves exist, especially in China and Indonesia [5].

Coal has sulfur in three primary forms: pyritic, organic, and sulfate [6]. Organic sulfur exists in several compounds, such as mercaptans, disulfides, thiophenes, thioethers, sulfoxides, and sulfonates. Conversely, inorganic sulfur is often found in pyrite and sulfates [7, 8]. The burning of coal produces sulfur oxides by the reactivity of sulfur compounds. Pyritic and sulfate sulfur decompose into inorganic oxides and sulfur dioxide during this process. The use of coal with a high gross calorific value (GCV) in thermal power plants is limited owing to its elevated sulfur content unless effective measures are used to control and diminish sulfur dioxide emissions. The physical extraction of inorganic sulfur from coal is economically feasible, although it fails to address the problem of organic sulfur properly [9]. Chemical desulfurization techniques are necessary to remove organic sulfur from coal due to the resilient nature of its macromolecular structure [10].

The efficacy of oxidizing agents in the desulfurization of coal is often limited, particularly in coal with elevated levels of organic sulfur [11]. Strong

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alkali or peroxyacetic acid may provide optimal desulfurization of organic sulfur; nevertheless, these agents are incapable of cleaving the C-S bond inside the thiophene ring, resulting in the degradation of coal's intrinsic properties related to its oxidative potential [12]. The effective desulfurization effect of organic sulfur could be realized by potassium tert-butoxide/hydrosilane for more than 60%. However, some of the organic sulfur was converted into sulfonate or sulfonic ester sulfur due to side reactions, which persisted in the coal matrix post-treatment, and their processing temperature constrained desulfurization efficiency [8].

Tetrahydrofuran (THF) is an appropriate solvent for the desulfurization process due to its ability to form hydrogen bonds and its inherent polarity [13]. THF participates in electrostatic interactions, depending on its polarity, with other ions and polar molecules. Interaction takes place between the regions of partial negative and partial positive charge in THF and these ions or polar molecules, leading to the creation of a three-dimensional sphere or hydration shell around the solute. This interaction promotes the breakdown of the solute. Thus, THF has been chosen in this investigation as a substitute for hydrosilane because of its efficacy in dissolving a wide variety of organic molecules [14]. The ultrasonics approach has been selected as a primary procedure in coal desulfurization, proving superior to ultrasonics treatment in isolation. Oxidative systems, consisting of potassium tert-butoxide and hydrosilane, have been particularly successful for sulfur removal from coal using ultrasonic waves [10]. Ultrasonic irradiation and treatment with potassium tert-butoxide/hydrosilane enhanced the hydrophobicity, surface area, and chemical adsorption of coal, as well as the wettability of pyrite [8].

Cheng et al. [4] examined the chemical impacts of coal desulfurization using peroxyacetic acid (PAA), concentrating on the generation patterns of hydroxyl radicals under ultrasonic circumstances by the iodine release method. The desulfurization rate and the hydroxyl radical production pattern were both determined to be precise. Their findings underscored the significance of the synergistic physical and chemical effects of ultrasonics in the desulfurization process. The generation of hydroxyl radicals significantly facilitated desulfurization by promoting the oxidation and elimination of pyrite, mercaptans, and sulfoethers, as shown by the hydroxyl radical production patterns identified by the iodine release technique.

The studies used the beneficial experimental design method called Design Expert to decrease both the cost and duration of the laboratory experiment. This software not only established the experiment and analyzed the data, but also generated graphical representations and enhanced the process with great efficiency [15]. Design Expert provides customers with a range of planning choices, enabling them to choose and merge elements with parameters [16, 17]. Upon the completion of the plan, it generates a run chart that presents the tests in a randomized sequence. The main objective of this revolutionary design method is to determine the connections between different aspects to optimize parameters and offer statistical frameworks. Diverse analytical methods were used to examine the characteristics of coal before to and during desulfurization, together with the formation pattern of hydroxyl radicals, to elucidate the mechanism of synergistic action. Various research has shown that oxidizing chemicals generally decrease the quantities of heterocyclic sulfur to a minimum [17-19]. While KOtBu successfully eliminated organic sulfur from coal, it proved to be inefficient in cleaving the C-S bond inside the thiophene ring, possibly impacting the fundamental characteristics of the coal.

The main objective of this experiment is to examine the desulfurization reductive effect of high-sulfur coal using ultrasonics with potassium tert-butoxide and tetrahydrofuran (KOTBU/THF). This study examines the best conditions for sulfur removal from high-sulfur coal, concluding that a solution of 25% w/v potassium tert-butoxide in tetrahydrofuran at 70 ˚C for 30 minutes is ideal. The samples' surface features were examined using Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (FESEM-EDX) to reveal the physical effects. Furthermore, the FTIR and TGA investigations discerned functional groups and modifications in thermal properties. The sonication method used in this study produces ultrasonic leaching shockwaves that create small fissures on the coal's surface, enhancing the reagent's access to the coal particles. The ideal concentration, temperature, and processing duration for the coal desulfurization process were determined using the Central Composite Design-Response Surface Methodology (CCD-RSM) to reduce the number of experimental trials.

EXPERIMENTAL

Chemicals and Materials

All the reagents were of analytical grade and used as received without purification. Potassium tert-butoxide (KOtBu, > 95%), tetrahydrofuran (THF > 98%), barium chlorite ($BaCl_2.H_2O$), nitric acid (HNO_3), standard ion Fe solution, potassium iodide (KI), and acetone (CH_3COCH_3).

Table 1. Characterization of raw coal.

Proximate analysis (wt.% db)		**Ultimate analysis (wt.% daf)**		**Forms of sulfur (wt.% db)**		**Calorific Value (MJ/kg)**
Ash	14.83	**Carbon**	61.26	**Total sulfur (Ts)**	3.94	25.49
Volatile matter	44.40	**Hydrogen**	5.03	**Sulfate sulfur (Ss)**	0.89	
Fixed carbon	40.77	**Nitrogen**	1.38	**Pyrite sulfur (Ps)**	1.36	
		Sulfur	3.94	**Organic sulfur*(Os)**	1.69	
		Oxygen*	28.39			

db = dry basis weight unit
daf = dry-ash-free basis weight unit
* = calculated by the difference

Coal Sample Preparation

The high-sulfur coal sample investigated in this study was originated from Jambi Province, Indonesia. To achieve particle sizes of 212 µm, the coal was ground into a fine powder and then screened using progressively smaller screens. The pulverized coal underwent sifting for 30 minutes using an Endecott Shaker Model EFL2 MK3, thereafter dried for 24 hours at 80 ˚C in a vacuum oven. The coal was stored in a well-sealed container to avert moisture penetration. **Table 1** displays the ultimate, proximate, and sulfur compositions of the raw coal [20].

Preparation of Potassium Tert Butoxide (KOtBu) Reagent

About 25 g of potassium tert-butoxide will be mixed with 100 ml tetrahydrofuran and added into the Schlenk tube (**Figure 1**). Then, the sample was purged with a nitrogen gas three times to make sure it is under inert condition. After that, the sample was stirred at 180˚ C for 80 minutes and conserved for further analysis as shown in **Figure 2**.

Chemical Desulfurization of Potassium Tert-Butoxide and Tetrahydrofuran

Chemical desulfurization was performed following the methodology outlined by Tang et al. [17] with some alterations shown in **Figure 2**. Approximately 5 g of raw coal (< 212 µm) was disseminated in a combination of potassium tert-butoxide and tetrahydrofuran, then purged with vacuum and nitrogen gas three times to provide an inert nitrogen atmosphere. Subsequently, the sample was agitated at 180 ˚C for 80 minutes and then subjected to ultrasonic energy at a frequency of 40 kHz, following the temperatures and durations specified in **Table 2**. After processing, the residual solution was filtered, rinsed with acetone, dried in a vacuum oven at 110 ˚C for three hours, and preserved for future analysis. The reaction was also performed with other weight-to-volume ratios of KOtBu to THF, namely 4.75%, 10%, 17.5%, and 25%.

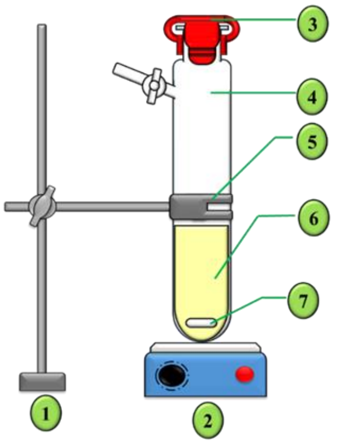

Figure 1. The experimental procedure of preparation of KOtBu reagent (1); retort stand (2); hot plate (3); suba-seal (4); Schlenk tube (5); clamp (6); KOtBu reagent (7); magnetic stirrer.

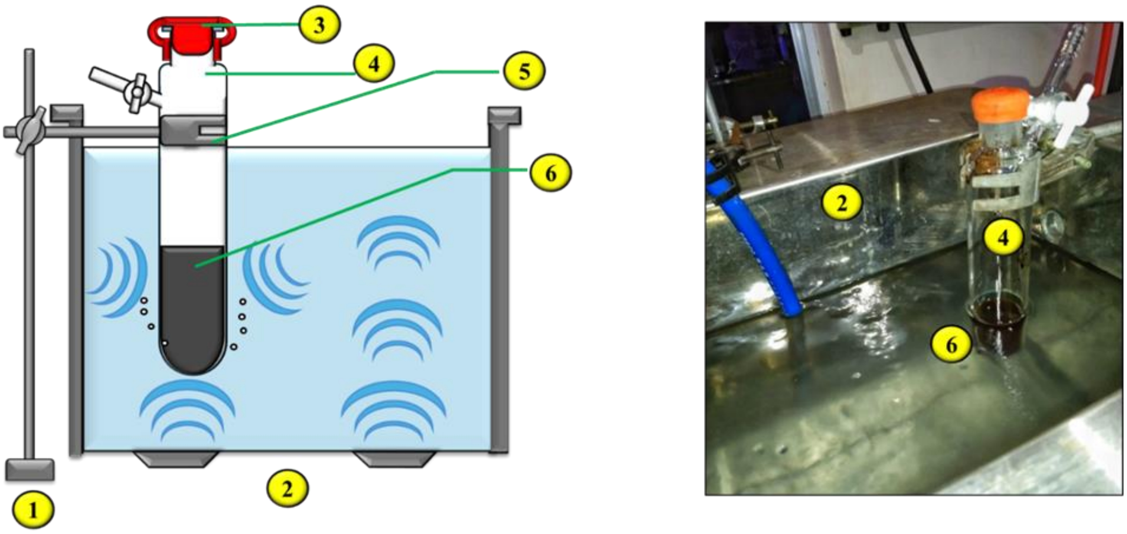

Figure 2. The experimental procedure for coal desulfurization of (a) illustrated and (b) real. (1); retort stand (2) sonicator (3); suba-seal (4); Schlenk tube (5); clamp (6); Coal+KOtBu reagent.

Table 2. List of variables, codes, and design coordinates.

Coded	Parameter	Units	Minimum	Maximum	-1 Actual	+1 Actual
A	Concentration	%	10	25	4.75	30.25
B	Temperature	˚C	30	70	16	84
C	Time	Min	10	30	3	37

All solutions were made and kept in sealed Schott bottles to prevent contamination and moisture ingress. **Table 2** contains a list of the optimization parameters, including concentration, temperature, and processing time. The experiment was conducted twice to get an accurate result. Under optimal conditions, the blank samples were generated by pre-treating coal with a mixture of KOtBu and THF.

Sulfur Assay Studies

Total sulfur (TS) in coal was analyzed using ASTM D3177-02 (2012) [21], whereas ASTM D2492-02 (2012) [22] was used to quantify sulfate sulfur (SS) and pyrite sulfur (PS). The organic sulfur (OS) was determined by removing the combined amounts of sulfate and pyritic sulfur from the total sulfur, as per Equation (1), while the percentage of organic sulfur removal was estimated using Equation (2) [20].

$$Os = Ts - (Ps + Ss) \qquad (1)$$

$$Percent\ Os\ removal\ (\% = (Ts - Os) / Ts\ x\ 100 \qquad (2)$$

Experimental Design

Three variables were selected to assess their influence on the percentage of organic sulfur removal from coal which are the concentration of potassium tert-butoxide (KOtBu), temperature (˚C), and time (minute). The variables denoted by the letters (A), (B), and (C) pertained to the study's findings about the percentage of organic sulfur removal in coal. The parameters were optimized using Central Composite Design (CCD) under Response Surface Methodology (RSM) in Design Expert V13, yielding 18 scheduled experimental trials. The studies were conducted randomly to reduce response errors. The variables A, B, and C are quantitative and vary within the ranges specified in **Table 2**. The influence of extraction parameters A, B, and C was evaluated using Design Expert V13. An analysis of variance (ANOVA) estimates the parameters A, B, and C, together with the response output, inside a quadratic polynomial model to evaluate the significance of each experimental parameter and their interactions throughout the desulfurization process [23]. The optimal conditions were derived from the generated response surface models.

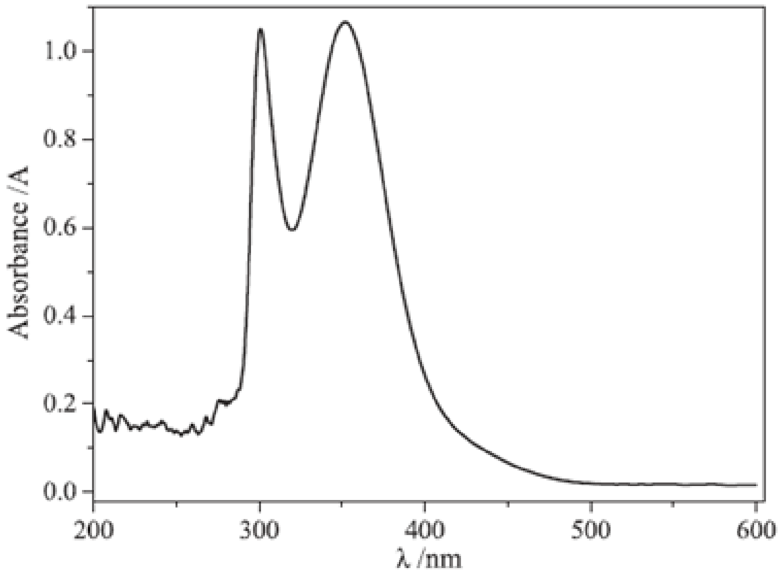

Figure 3. The absorption spectra of KI solution after ultrasonic irradiation.

Hydroxyl Radical Production

The iodine release method was executed as per the procedures identified by Tang et al. [17] to generate hydroxyl radicals (·OH) under ultrasonic conditions and to monitor the absorbance variation of potassium iodide (KI) solution using an ultraviolet spectrophotometer (2802 uv/vis) post-ultrasonic irradiation. The untreated aqueous solution of KI used as a reference to guarantee comparability. **Figure 3** reveals two peaks at 306 nm and 354 nm; however, the peak at 354 nm had a larger profile, and its absorbance was directly proportional to the ion concentration. The ion concentration pertains to the iodine concentration in the presence of potassium iodide [24]. Consequently, the absorbance at 354 nm was used to quantify the iodine content [20].

Characterization Method

Analysis of Field Emission Scanning Electron Microscopy (FESEM-EDX)

Field emission scanning electron microscopy (FESEM) is a non-destructive technique used to analyze micron-scale particle size and surface properties [25]. The FESEM (Oxford Instrument Max 20) was used to analyze the high-sulfur coal and treated coal samples using SEM-EDX to evaluate the microstructural changes induced by the thermal cracking of organic components in coal, utilizing the EDX attachment. The SEM images were captured at magnifications between 7,000X and 100,000X. FESEM images and EDX spectra displaying peaks of several elements were acquired throughout the coal desulfurization process [24].

Analysis of Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed on both raw and treated coal to determine and compare the changes in functional group absorption peaks in each sample. The sample was dehydrated overnight at 80 °C before FTIR measurement to prevent moisture influence. The coal samples were crushed with KBr at a mass ratio of 1:1000 and shaped into tiny pellets. A Perkin Elmer FTIR Spectrometer was used, including a scan range of 400-4000 cm^{-1}, with 64 scans conducted at a resolution of 4 cm^{-1} [24].

Thermogravimetric Analysis (TGA)

The thermal behavior changes of the raw and treated coals were analyzed using a thermogravimetric analyzer (Netzsch TG 200 F3 Tarsus). Each coal sample, weighing 5-10 mg, was placed in an alumina pan inside an argon atmosphere at a flow rate of 100 mL/min [26]. The pyrolysis of the processed coal was performed in an argon environment, with temperatures varying from 20 to 1000°C and a heating rate of 20 °C/min. TGA experiments were performed twice to ensure the repeatability of results [27].

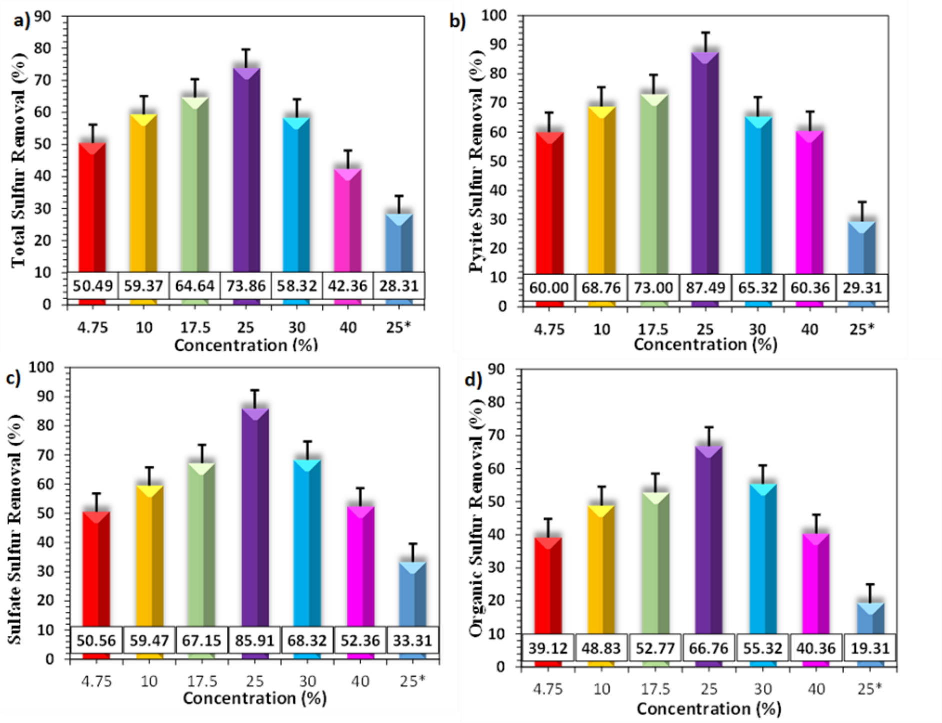

Figure 4. Total sulfur (a) and form of sulfur, (b) pyritic, (c) sulfate and (d) organic sulfur removal as a function of different KOtBu concentration ratio (%), reaction time (30 min), temperature (70 °C). KOtBu: potassium tert-butoxide.

RESULTS AND DISCUSSION

Effect of KOtBu Concentration on Desulfurization of Coal

The concentration of potassium tert-butoxide affects the desulfurization of coal, as evident in **Figure 4**. As shown in **Figure 4(a)**, as the concentration ratio of KOtBu increased from 4.75% to 25%, the percentage of total sulfur removal increased from 50.49% to 73.86%. Similarly, for pyritic sulfur, when the concentration increased, the percentage of sulfur removal increased from 60% to 87.49% followed by sulfate sulfur and organic sulfur in **Figure 4(b)**, **Figure 4(c)** and **Figure 4(d)**.

The decrement in sulfur content with increment in concentration can be attributed to the solubilization of the sulfates, conversion of pyritic and some organic functional groups like thiols, and disulfide, present in the coal to soluble salts [28]. The growth tendency of desulfurization decreased as the concentration exceeded 25%. Furthermore, high concentration of KOtBu reduced the economic efficiency, so 25% was considered as the value of concentration. This also has been compared with the conventional method (stir) with the percentage of concentration being same with the ultrasonic method, but it shows that the ultrasonic method is better than conventional methods as the percentage of concentration is lower than the ultrasonic method [29].

Figure 5 shows the effect of ultrasound on hydroxyl radical production. A 0.2 M potassium iodide (KI) solution was exposed to various reagent volume mixing ratios [30] and the finding was proved by the maximum removal of total sulfur (73.86 %) as depicted in **Figure 5(a)**. As shown in **Figure 5(b)**, at a concentration of 4.75%, the curve's slope was minimal, indicating that the production rate of hydroxyl radicals per unit of time was at its lowest. The slope of the curves increases with a higher concentration ratio, indicating that the production rate of free radicals climbs until it reaches a maximum at 25%, after which it decreases [20]. All of this suggests that the absorbance factor corresponded with the established pattern of desulfurization degree variation [31].

The pertinent laws of ultrasonography were associated with this outcome. The researchers also indicated that the concentration of additives augmented the generation of cavitation bubbles from the ultrasonic wave, hence enhancing the physical and chemical impacts of cavitation, which facilitates the desulfurization process [32]. This has led to the accumulation of many cavitation bubbles, producing a bubble shielding effect that diminishes the conversion efficiency of ultrasound [33].

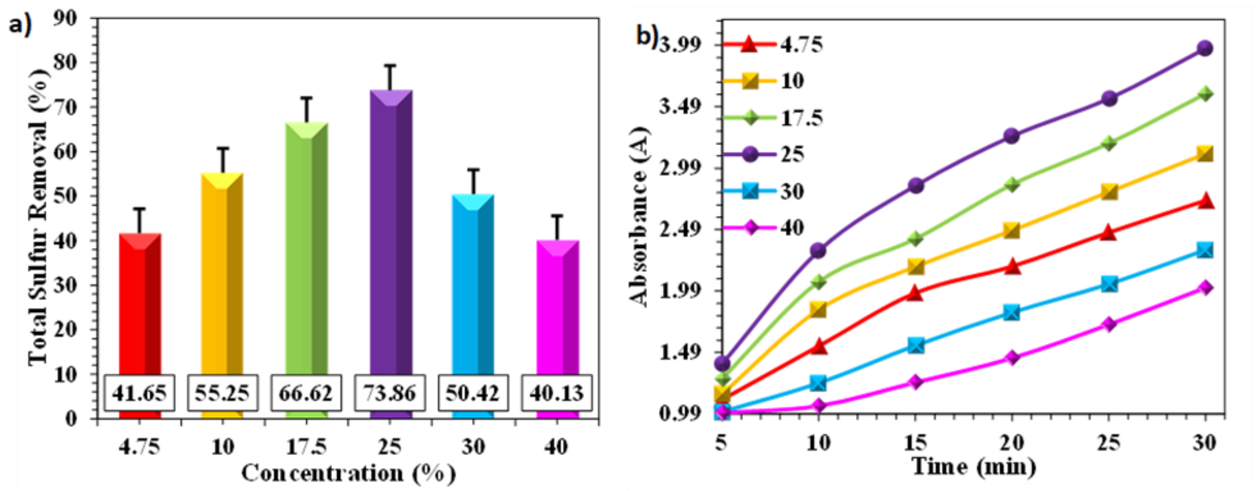

Figure 5. Effect of concentration on the total sulfur removal (a) and the production of ·OH (b), temperature (70˚C), sonication time (30 minutes).

Effect of Processing Temperature on Desulfurization of Coal

Figure 6 illustrates that the percentage of sulfur removal escalated rapidly with rising processing temperatures, indicating that elevated temperatures significantly enhance the reductive desulfurization reaction. Thus, processing temperature is a critical factor influencing coal desulfurization [34]. According to **Figure 6(a)**, the sulfur removal percentage for organic sulfur removal rose to 66.76% when the processing temperature was maintained at 70 °C. Nonetheless, the increasing trend diminished when the processing temperature above 70 °C. This results from the fast diffusion of solvent molecules at elevated temperatures into the coal sample, leading to an enhanced sulfur removal percentage [35]. Increasing temperature could effectively accelerate the sulfur removal reaction and it shows that the processing temperature was one of the factors of affecting desulfurization degree.

Similarly, the percentage of TS removal, PS removal and SS removal also increases as the temperature increases exceeding 70 °C, according to **Figure 6(b)**, **Figure 6(c),** and **Figure 6(d)** respectively. As the comparison of the methods, the percentage of sulfur removal using ultrasonics is higher than the conventional method using the stirred method. **Figure 6(a)** indicates that the sulfur removal percentage for OS removal increased to 66.76% at a processing temperature of 70 °C. However, the upward tendency decreased when the processing temperature above 70 °C. This occurs due to the rapid diffusion of solvent molecules at increased temperatures into the coal sample, resulting in a higher proportion of sulfur removal [36]. Moreover, in accordance with the reaction tank's limits regarding high temperature acceptance [37], 70 °C was selected as the optimal processing temperature. As the comparison of the methods, the percentage of sulfur removal using ultrasonic is higher than the conventional method using the stirred method.

From this analysis, the peak generation of OH occurred at 70 °C, confirmed by the highest TS removal at that temperature as observed in **Figure 7(a)**. Meanwhile, **Figure 7(b)** illustrates the absorbance curves at different temperatures. The slope of the curve escalates with a temperature rise of 70 °C. Tang et al. [17] found that temperature initially facilitated the production of cavitation bubbles; however, when the pressure inside the bubbles increased, the rupture of the bubbles became worse after the temperature above 70 °C [20].

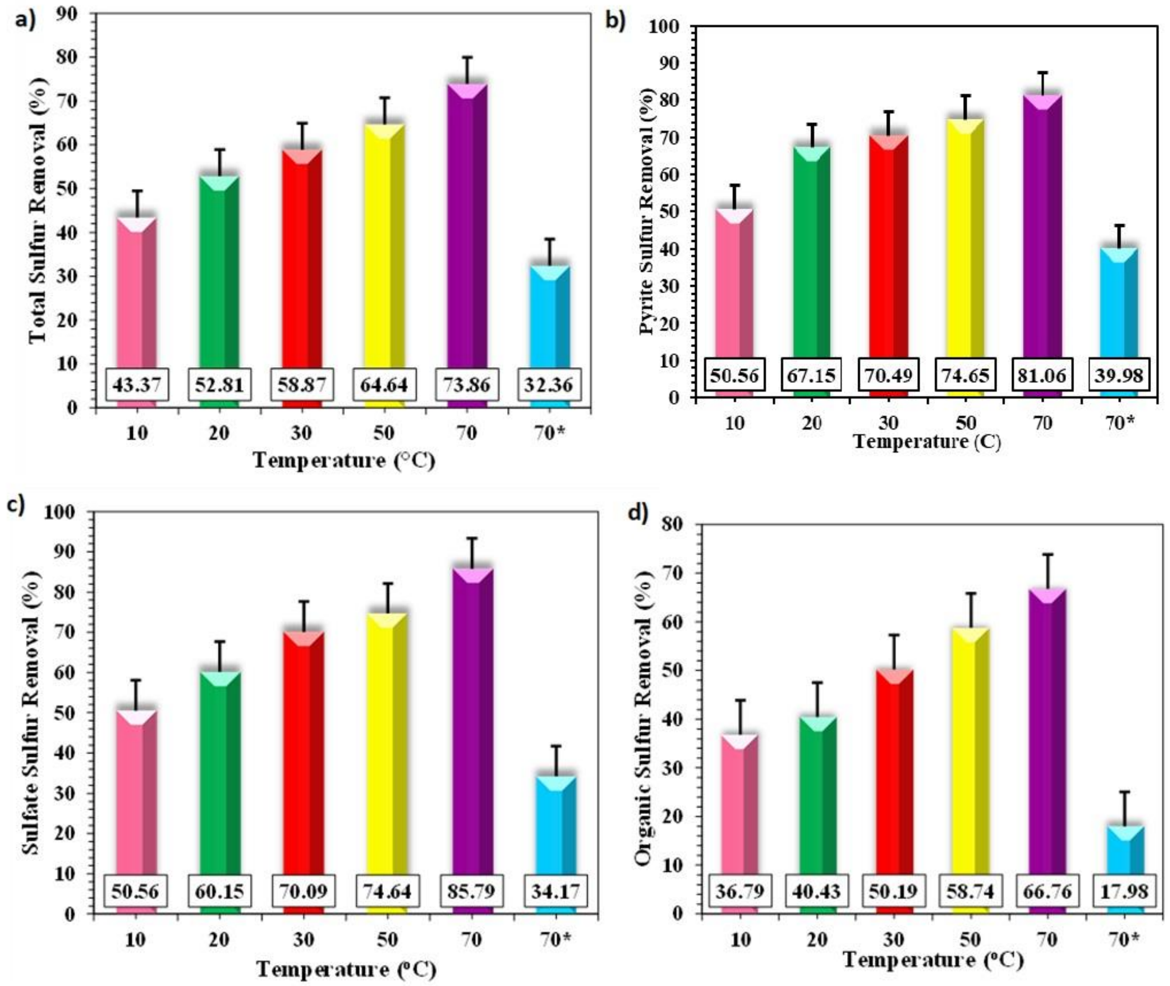

Figure 6. Total sulfur (a) and form of sulfur, (b) pyritic, (c) sulfate and (d) organic sulfur removal as a function of different temperature, KOtBu concentration ratio (25%), processing time (30 minutes). KOtBu: potassium tert-butoxide.

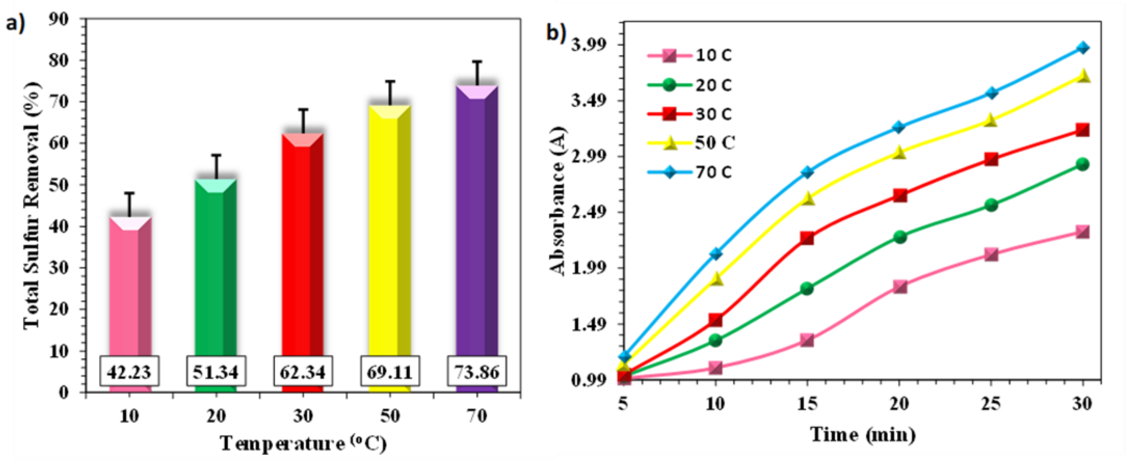

Figure 7. Effect of ultrasonic temperature on the (a) total sulfur removal and (b) the production of ·OH, KOtBu concentration (25%), sonication time (30 minutes).

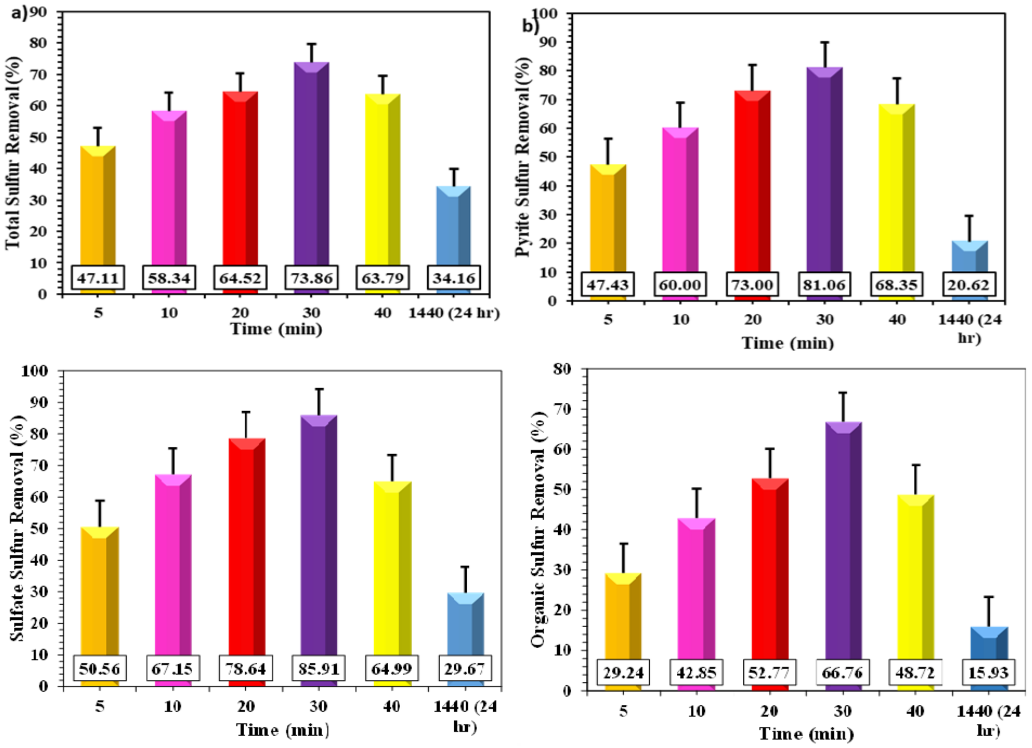

Figure 8. Total (a) sulfur (b) pyritic, (c) sulfate and (d) organic sulfur removal as a function of different time, KOtBu concentration ratio (25%), temperature (70 °C).

Effect of Processing Time on Desulfurization of Coal

As shown in **Figure 8(a)**, for TS removal, the maximum increments of 73.86% occurs at 30 minutes. Similarly for PS removal in **Figure 8(b)**, the maximum sulfur removal of 81.06% is observed at 30 minutes, and for SS removal in **Figure 8(c)**, the maximum sulfur removal of 85.91% occurs at 30 minutes respectively. Besides, as processing time increased from 5 to 30 minutes, the desulfurization removal for organic sulfur removal increased from 29.24% to 66.76%, while the growth tendency reduced at the same time as shown in **Figure 8(d)**. The appropriate extension of treatment duration facilitated the complete reactivity of sulfur atoms with the reductive agent, hence enhancing desulfurization efficiency [38], therefore, 30 minutes was considered as the appropriate processing time. However, in comparison with the method, the ultrasonic method is higher in the percentage of sulfur removal than the conventional method (stirred method). The ultrasonic wave caused cavitation bubbles in the additives, enhancing the physical and chemical effects of cavitation, which facilitated the desulfurization procedure [39].

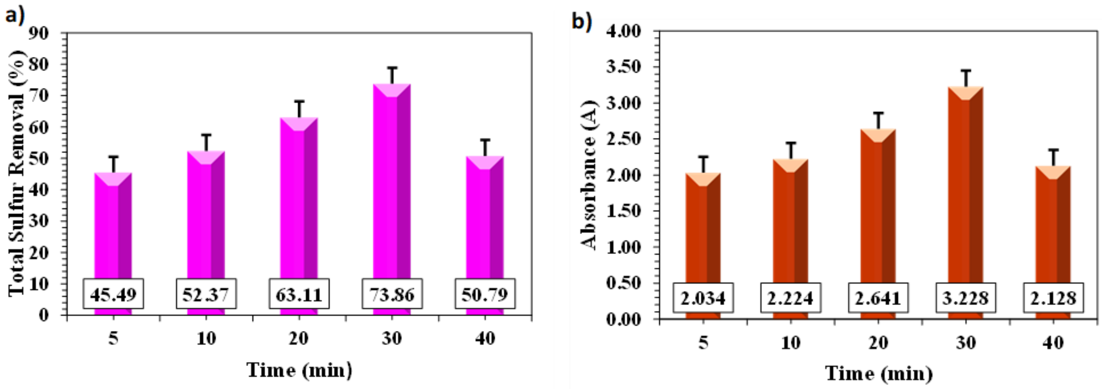

Figure 9. Effect of ultrasonic temperature on the (a) total sulfur removal and (b) the production of OH, KOtBu concentration ratio (25%), temperature (30 °C).

The influence of time on the overall sulfur reduction is shown in **Figure 9(a)**. According to **Figure 9(b)**, comparable tendencies were seen in the influence of time on hydroxyl radical generation; as time increased, the slope of the curve first rose and then declined after 30 minutes. The peak generation rate of OH was achieved at 30 minutes. When the duration ranged from 5 to 30 minutes, the desulfurization efficiency exceeded 73.86%. As time progressed, desulfurization started its fall [40]. Mao et al. [29] observed that as time progressed, the pulp temperature first rose rapidly before stabilizing. The activity of nascent oxygen and ·OH radicals generated by ultrasonic chemical processes is enhanced due to the elevated pulp temperature, which accelerates the oxidation of surface sulfur, resulting in the formation of sulfoxide units in the pulp [20, 41].

Development of the RSM Model

ANOVA is used to assess statistical variables for regression analysis. **Table 3** presents the experimental matrix and encoded values of the parameters. **Table 4** presents the experimental runs, experimental values, and RSM values [42]. Equation (2) delineates the empirical correlation between the percentage of organic sulfur removal and the process parameters. Negative indications indicate antagonistic effects, whilst positive signs signify synergistic benefits [16, 43].

$$\text{Organic Sulfur Removal \%: } 42.17 + 4.60A + 3.44B + 2.33C + 2.42AB - 1.56AC + 8.26A^2 + 1.63B^2 + 0.9924\,C^2 \qquad (2)$$

A, B, C and D are the optimized parameters that represent KOtBu concentration, temperature, and processing time, respectively.

Table 3. Experimental variable and coded levels for central composite design.

Factor	Name	Min.	Max.	Coded low	Coded high	Mean	Std. deviation
A	Concentration (%)	4.75	25.00	-1 ↔ 10.00	+1 ↔ 25.00	16.83	5.79
B	Temperature (°C)	16.00	84.00	-1 ↔ 30.00	+1 ↔ 70.00	50.00	17.50
C	Time (minutes)	3.00	37.00	-1 ↔ 10.00	+1 ↔ 30.00	20.00	8.75

Table 4. Experimental factors along with experimental and RSM response.

Std	Run	Factor 1 A: Concentration Percentage	Factor 2 B: Temperature (°C)	Factor 3 C: Time (min)	Response 1 Organic Sulfur (%)
12	1	17.5	50	3	42.53
7	2	10	70	30	55.22
11	3	17.5	84	20	52.77
6	4	25	30	30	50.45
19	5	17.5	50	20	42.37
9	6	4.75	50	20	59.42
10	7	17.5	16	20	42.19
13	8	17.5	50	37	48.74
2	9	25	30	10	52.30
15	10	17.5	50	20	46.30
18	11	17.5	50	20	40.88
5	12	10	30	30	48.83
4	13	25	70	10	60.37
17	14	17.5	50	20	39.16
8	15	25	70	30	66.76
14	16	17.5	50	20	43.75
3	17	10	70	10	42.85
16	18	17.5	50	20	40.43
1	19	10	30	10	44.19

Statistical Design

The main explanation for conducting tests randomly was dictated by the two-level factorial design. According to the plan, 19 tests were conducted, which were demonstrated in **Table 4**.

The major justification for doing tests randomly was determined by the two-level factorial design. According to the design, 19 tests were performed, as seen in **Table 4**. A variance analysis was performed to assess the influence of the effects and interactions among the variables. The same table displays the ANOVA analysis for high sulfur coal. The ANOVA analysis indicates that the parametric factors substantially affect the sulfur removal from the coal sample. The F-value is less than or equal to 0.05, indicating that the variables have a substantial impact on sulfur removal from coal. Conversely, they are rejected [16].

An accuracy ratio of 16.137 indicates a suitable signal, allowing the model to support design space exploration. The 'Lack of Fit' F-value of 0.32 signifies the insignificance of pure error, with an 85.50% possibility that this F-value may arise from random fluctuation. The ANOVA data, obtained from Equation (2), is shown in **Table 5**. P-values less than 0.0500 signify the significance of model conditions, with A, B, and C being the primary model conditions of KOtBu concentration [16]. Values beyond 0.1000 indicate the insignificance of model conditions. If any words had been briefed, it would have been necessary to diminish the model terms; nevertheless, this was not applicable in our cases [44].

The tolerability of the developed model was the criteria for evaluating the validity of the experimental results (**Figure 10**). **Figure 10(a)** shows the correlation between externally studentized residuals and anticipated sulfur removal percentage. **Figure 10(b)** illustrates the acceptable probability and studentized residuals. **Figure 10(c)** shows the relationship between the observed and anticipated rates of sulfur elimination. No identifiable problems with normality were seen. This signifies that the variance of actual observations is stable, therefore rendering the change of response variables unnecessary. The R-squared value was 0.9611, whereas the adjusted R-squared value was 0.9223 [16].

Table 5. ANOVA for response surface quadratic model for sulfur removal from coal.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	p-value	Source
Model	1034.69	9	114.97	24.74	< 0.0001	significant
A-Concentration	188.96	1	188.96	40.66	0.0001	
B-Temperature	163.16	1	163.16	35.10	0.0002	
C-Time	74.81	1	74.81	16.10	0.0031	
Residual	41.83	9	4.65			
Cor Total	1076.52	18				

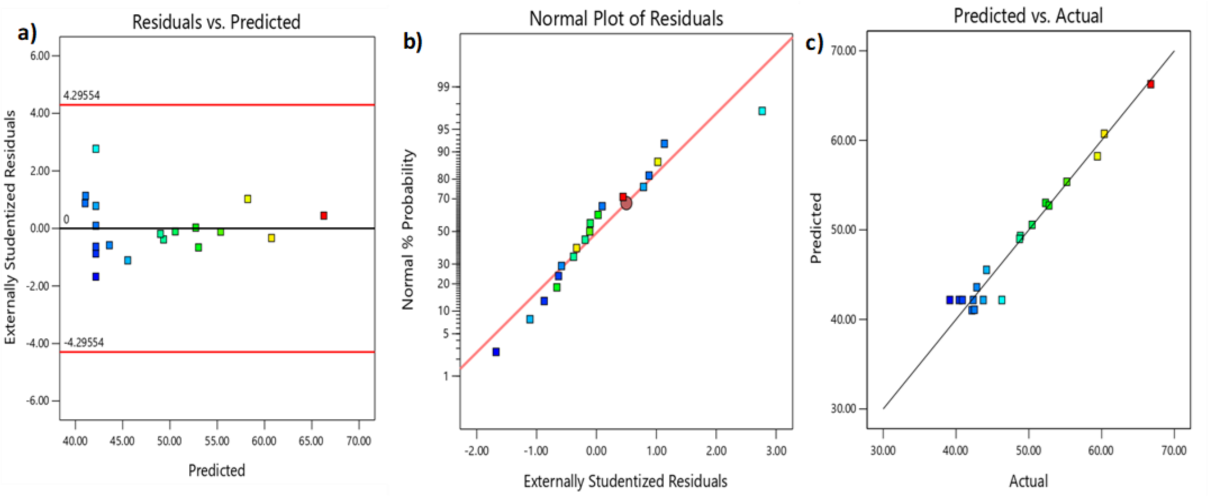

Figure 10. Plots of (a) Predicted sulfur removal vs studentized residuals, (b) studentized residuals vs percentage probability and (c) Experiment sulfur removal vs Predicted sulfur removal.

Table 6. Model statistical parameters obtained from ANOVA [16].

Insignificant factors excluded	Sulfur removal (%)
Standard deviation	2.16
Mean	48.40
Coefficient of variance	4.45%
Adequate precision	16.1368
R^2	0.9611
Adjusted R^2	0.9223
Predicted R^2	0.8774

The standard deviation was 2.16, the mean was 48.40, and the coefficient of variance was 4.45%. **Table 6** displays the statistical results obtained from ANOVA regarding sulfur removal.

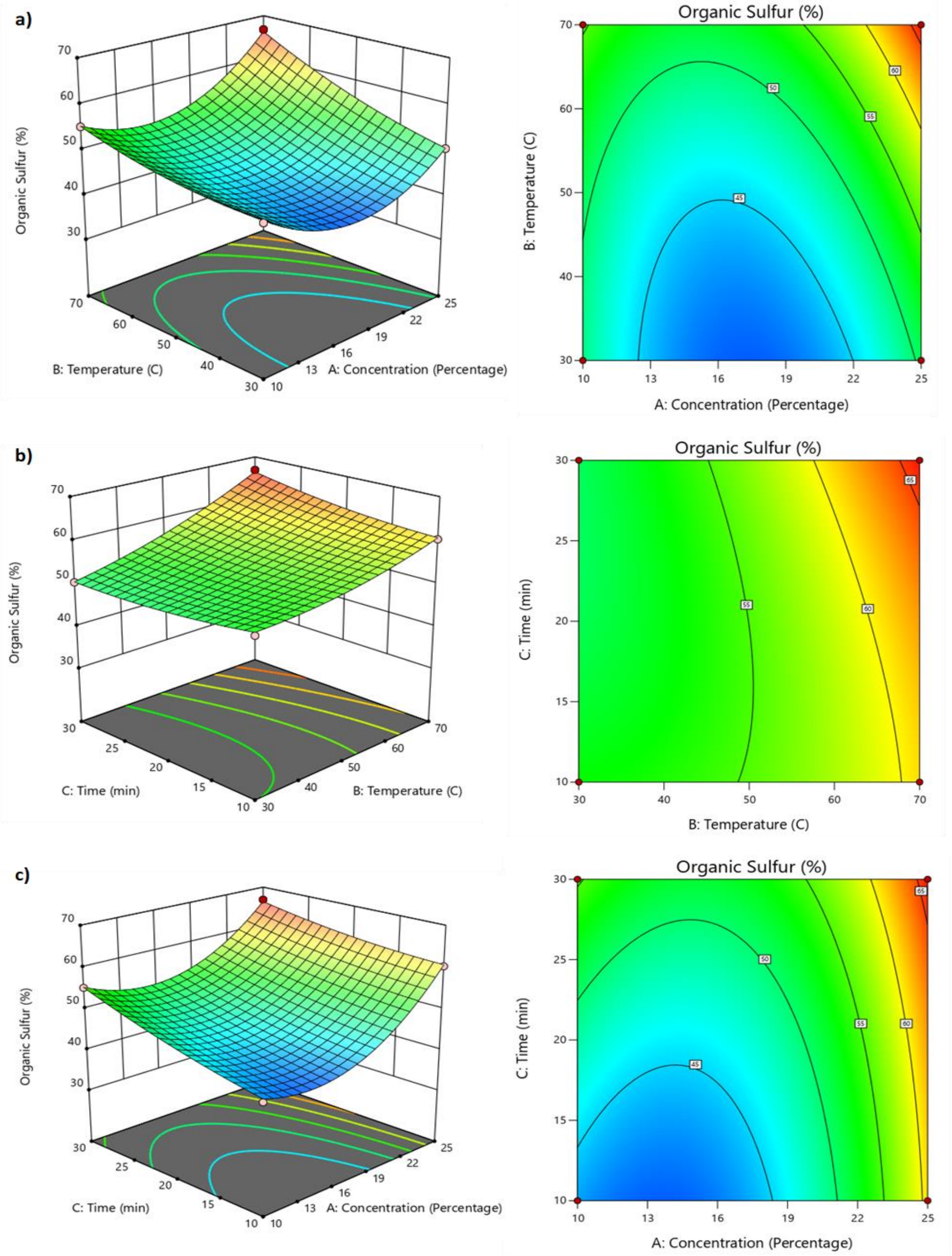

Figure 11. Combined Effect of (a) KOtBu Concentration and Temperature, (b) Temperature and Time, (c) KOtBu Concentration and Time.

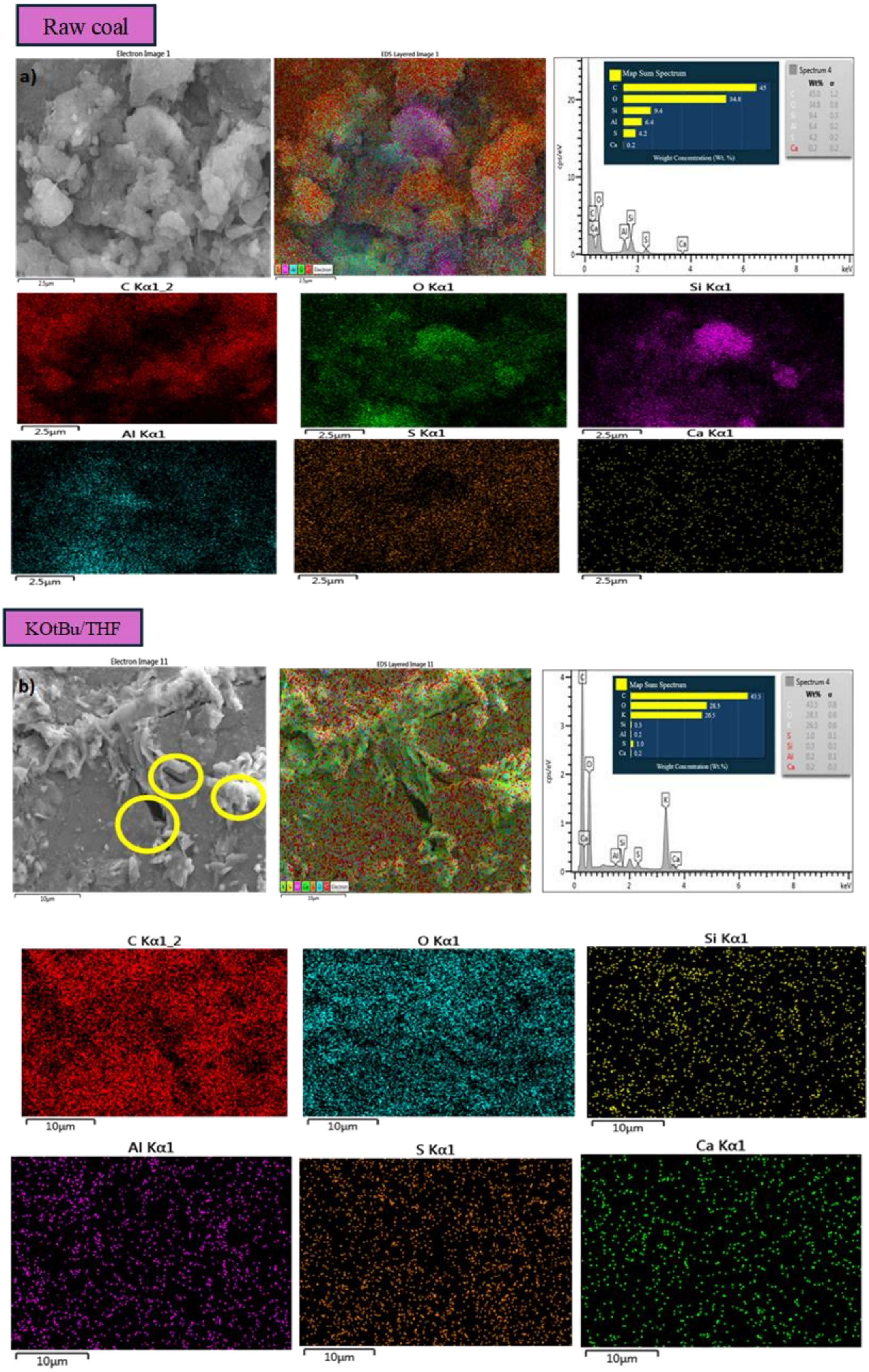

Figure 12. SEM image showing the elemental composition mapping of (a) sulfur in raw coal and (b) sulfur in treated coal under optimal conditions for 30 minutes at 70 °C.

Combined Effects of Time, Temperature and KOtBu Concentration on Sulfur Removal

Three-dimensional graphs were generated using response surface methodologies to depict the aggregate effect of many variables on sulfur removal. The synergistic effects of KOtBu concentration and temperature, temperature, and duration, and KOtBu concentration and duration on the desulfurization process is shown in **Figure 11(a)**, **Figure 11(b)**, and **Figure 11(c)** respectively.

Response surface approach was used to examine the individual and synergistic impacts of parametric parameters on the sulfur removal percentage from coal [41]. Three-dimensional graphs depict the impact of different parameters on sulfur removal. All three parameters analyzed were found to influence sulfur removal. **Table 2** demonstrates that KOtBu concentration is the primary factor affecting coal desulfurization, as shown by its highest F-value. Other parameters, like temperature and duration, are of less importance in this context. The figures indicate that the desulfurization process improves with higher concentrations of KOtBu, heightened temperature, and extended processing duration [16].

Optimum Conditions by Response Surface Modeling

The optimum conditions for the sulfur removal are KOtBu concentration of 25% KOtBu, a temperature of 70 °C, and time of 30 minutes. The sulfur removal at optimum condition is 66.76%.

CHARACTERIZATION

Effect of KOtBu/THF Treatments on the Microstructure of the Coal

Figure 12(a) and **Figure 12(b)** illustrate the effects of KOtBu/THF treatments on the microstructure of untreated and treated coal, respectively, at optimal conditions of 25% concentration, a treatment duration of 30 minutes, and a temperature of 70 °C. **Figure 12(b)** shows SEM images of the treated coal, revealing the presence of surface voids. The findings are likely attributable to pyrite extraction and selective mineral dissolution from the coal surface, as demonstrated in a study by Rawat and Yadav [25]. Furthermore, the research identifies the inorganic elements acquired using SEM-EDX after the removal of carbon and oxygen, which allows for the differentiation of their characteristics [45]. The SEM-EDX examination revealed that raw coal included a reduced carbon percentage, while demonstrating a substantial presence of sulfur and oxygen, with a negligible amount of silica and alumina minerals. The EDX investigation indicated a decrease in sulfur content in the treated coal, since the sulfur-bearing minerals were completely soluble after desulfurization, as seen in **Figure 12(b)** [46]. The highest carbon content was observed at optimum circumstances, suggesting that a greater number of mineral constituents (silica and alumina) was removed prior to the raw coal [20, 47].

Fourier Transform Infrared Spectroscopy (FTIR) of the Optimized Sample

Figure 13 illustrates the FTIR spectra of coal that has undergone KOtBu/THF treatment in contrast to untreated coal. Absorption peaks at 1420 cm^{-1} and 2525-2600 cm^{-1} may signify the existence of thiophene rings and thiol (S-H stretch) in raw coal, respectively [48]. The diminution of the aromatic ring is shown by the peak within the region of 1450–1615 cm^{-1} [49]. Absorption peaks at 1330–1125 cm^{-1} and 1060–1030 cm^{-1} indicate the presence of sulfoxide (S=O) and sulfone (O=S=O) [50]. The stretching vibrations of the C-S and S-S disulfide bonds are shown by peaks at 705-570 cm^{-1} and 620-600 cm^{-1}, respectively [30]. The peaks seen between 843-600 cm^{-1} correspond to the inorganic and organic mineral constituents of coal, demonstrating that the KOtBu/THF successfully eliminated these materials [20].

The peaks at 843-600 cm^{-1} correspond to the inorganic and organic mineral constituents in coal, indicating that these components were swiftly removed during the pre-treatment procedure [51]. The thiophene, disulfide (C-S and S-S bonds), aromatic ring (C=C-C), and sulfoxide peaks of treated coal exhibited alterations and shifts towards higher wavenumber values, indicating a decrease in molecular mass compared to the peaks of raw coal. The absorption peaks of sulfone (O=S=O), sulfoxide (S=O), and disulfide (C-S and S-S) in coal were insufficiently pronounced and obscured by other oxygen-containing groups, leading to FTIR spectra that were too weak for identification. In conclusion, coal treated with KOtBu/THF may improve the extraction of organic sulfur compared to untreated coal [20, 52].

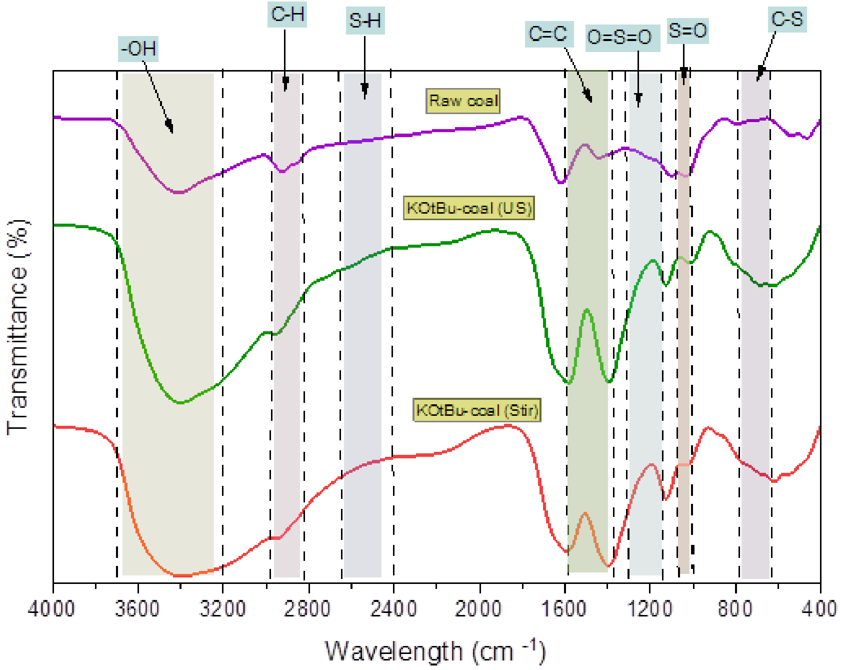

Figure 13. FTIR results of raw coal and coal with KOtBu/THF (25%) at 70°C for 30 minutes.

Changes in Thermal Properties of Coal

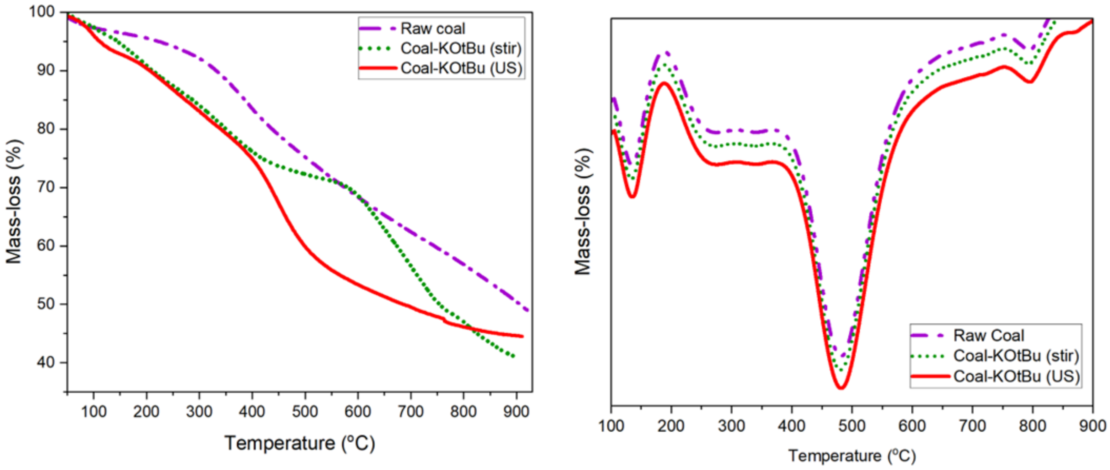

Figure 14. TGA and DTG curves of raw and treated coal samples.

TGA Profiles

The weight loss profiles of coal samples may be obtained using various KOtBu/THF treatment procedures using TG analysis. **Figure 14** illustrates the TGA and DTG profiles for untreated coal and two treatment processes: ultrasonics and conventional techniques. The pyrolysis of high-sulfur coal may be examined in three phases. The first phase involves the elimination of surface water or moisture, accompanied by some depolymerization conversion. Moisture discharge commenced in this experiment at temperatures ranging from 100 °C to 180 °C [53]. The second stage involves a response resulting in a weight loss of 40% - 50%. The residue degraded, resulting in a decreased rate of weight loss, while the residue ratio approached constancy at the conclusion, as seen in the figure. **Figure 14(a)** clearly demonstrates that the weight reduction of the coal sample transpires when volatile substances are emitted from 200 °C to 550 °C. The TG curves migrate to higher temperature regions as the heating rate rise [54]. The devolatilization phase started at 200 °C and continued up to a temperature range of 500 °C. The process of expelling solid residue from samples began at a temperature of 500 °C. Substantial devolatilization transpires during the temperature range of 200 °C to 600 °C, recognized as the active pyrolysis zone [55].

In TGA, the final solid residue weight increases with a rise in sample weight. In the active pyrolysis zone, the pyrolysis process is accelerated, leading to the production of a solid residue (charcoal) while the volatile component markedly diminishes. Devolatilization terminates at the temperature limit of 600 °C. The area where weight loss halts is known as the passive zone [56]. In this region, carbon and ash constituted the ultimate solid residue.

DTG Profiles

The peak temperature in the DTG curves reflects the highest rate of weight decrease. **Figure 14(b)** depicts the temperature and derivative of TG curves for high-sulfur coal samples following various treatments. The ultrasonic method elevates the reaction zone and the peak pyrolysis rate to an increased temperature. The most substantial weight loss in the sample occurs at the highest temperature, shown as the peak value on the DTG curves [57]. The final solid residue of high-rank coal diminishes with the traditional approach, but the ultrasonic process yields a greater percentage of solid residue. The thermal degradation of high-sulfur coal samples starts at temperatures above 150 °C, although it remains incomplete even at 900 °C owing to their composition. Consequently, the premium coal samples must be subjected to roasting at 950 °C to eliminate all volatiles and carbon [58]. The ultimate weight of residue produced during isothermal pyrolysis is influenced by the release of volatiles from the samples and the partial oxidation of the sample material.

CONCLUSION

In conclusion, KOtBu/THF effectively eliminated organic sulfur from the coal. The testing findings indicated that all concentrations (25%), temperatures (70 °C), and durations (30 minutes) could remove over 60% of organic sulfur. Additionally, many branched alkanes in the coal matrix underwent conversion into lower molecular weight fragments by C–C bond cleavage, resulting in an augmented mass loss during coal pyrolysis. Despite alterations in the amounts of carbon-containing functional groups due to the reduction effect, the fundamental aromatics within the macromolecular structure of coal remained mostly unaltered post-treatment. Consequently, the reduction of oxidized carbon atoms in the O–C–O, C-O, or O-C–O groups, together with side reactions and the fragmentation of branching chains, results in alterations to the properties of coal after the removal of organic sulfur from its macromolecular structure. These findings provide a foundation for investigating efficient and targeted methods for sulfur extraction from coal particles. KOtBu/THF techniques have good robustness under practically relevant conditions, including the presence of impurities in bulk reagents, as well as water and air and is currently being investigated for application in an industrial refining setting. Additional investigations using an X-ray photoelectron spectrometer (XPS) and X-ray diffraction analysis (XRD) are essential to ascertain the specific kind of organic sulfur eliminated in this work, since some organic sulfur compounds with a heterocyclic structure are challenging to extract from coal. Efforts are also underway to modify the KOtBu/THF method for a continuous flow system and to identify appropriate solutions for silane recycling and enhancing reagent efficiency overall.

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REFERENCES

1. Tao, X., Xu, N., Xie, M. and Tang, L. (2014) Progress of the technique of coal microwave desulfurization. *International Journal of Coal Science & Technology*, **1**, 113–128.

2. Zhang, F., Guo, H., Liu, Y., Liu, F. and Hu, R. (2020) Theoretical study on the desulfurization mechanisms of thiophene and benzothiophene under inert and oxidative atmospheres. *Fuel*, **280**, 118683.

3. Liu, J., Wang, Z., Qiao, Z., Chen, W., Zheng, L. and Zhou, J. (2020) Evaluation on the microwave-assisted chemical desulfurization for organic sulfur removal. *Journal of Cleaner Production*, **267**, 121878.

4. Cheng, G., Li, Y., Cao, Y. and Zhang, Z. (2023) A novel method for the desulfurization of medium–high sulfur coking coal. *Fuel*, **335**, 126988.

5. Grossman, S. L. (2023) The seaborne thermal coal market: volatile present and uncertain future. *The Coal Handbook*, *Woodhead Publishing*, 167–184.

6. Ken, B. S. and Nandi, B. K. (2018) Effect of some operational parameters on desulphurization of high sulphur Indian coal by KOH leaching. *Energy Exploration & Exploitation*, **36(6)**, 1674–1691.

7. Tang, L., Wang, S., Zhu, X., Guan, Y., Chen, S., Tao, X. and He, H. (2018) Feasibility study of

reduction removal of thiophene sulfur in coal. *Fuel*, **234**, 1367–1372.

8. Tang, L., Chen, S., Gui, D., Zhu, X., He, H. and Tao, X. (2020) Effect of removal organic sulfur from coal macromolecular on the properties of high organic sulfur coal. *Fuel*, **259**, 116264.

9. Xia, W. and 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.

10. Tang, L., Chen, S., Wang, S., Tao, X., He, H., Zheng, L., Ma, C. and Zhao, Y. (2018) Heterocyclic sulfur removal of coal based on potassium tert-butoxide and hydrosilane system. *Fuel Processing Technology*, **177**, 194–199.

11. Saikia, B. K., Khound, K., Sahu, O. P. and Baruah, B. P. (2015) Feasibility studies on cleaning of high sulfur coals by using ionic liquids. *International Journal of Coal Science & Technology*, **2**, 202–210.

12. Mesroghli, S., Yperman, J., Reggers, G., Jorjani, E. and Carleer, R. (2016) Impacts of sonication and post-desulfurization on organic sulfur species by reductive pyrolysis. *Fuel*, **183**, 278-291.

13. Madasu, J., Shinde, S., Das, R., Patel, S. and Shard, A. (2020) Potassium tert-butoxide mediated C–C, C–N, C–O and C–S bond forming reactions. *Organic & Biomolecular Chemistry*, **18(41)**, 8346–8365.

14. Sun, W., Liang, Y., Li, Q., Li, Z., Zhao, Z., Zheng, X., Wang, M., Liu, S. and Wu, Z. (2024) Experimental study on effects of tetrahydrofuran soaking on pore structure and gas adsorption and desorption characteristics of coal. *Powder Technology*, **445**, 120117.

15. Behera, S. K., Meena, H., Chakraborty, S. and Meikap, B. C. (2018) Application of response surface methodology (RSM) for optimization of leaching parameters for ash reduction from low-grade coal. *International Journal of Mining Science and Technology*, **28(4)**, 621–629.

16. Anwar, F., Nasir, R., Maqsood, K., Suleman, H., Rehman, F., Ali, A., A., Abdulrahman, A., and Mahfouz, A. B. (2020) Desulfurization and optimization of low-grade local coal by sequential KOH and HCl treatment. *Journal of Sulfur Chemistry*, **41(1)**, 44–56.

17. Tang, L., Fan, H., Guo, J., Zeng, W. and Tao, X. (2018) Investigation on the mechanism of coal desulfurization by ultrasonic with peroxyacetic acid. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **40(8)**, 999–1009.

18. Rehman, F., Ahmad, S. W., Zafar, M. S., Ahmad, S., and Zia-Ul-Haq, M. (2018) Parametric optimization of coal desulfurization through Alkaline leaching. *Polish Journal of Chemical Technology*, **20(3)**, 103–109.

19. Liu, Q., Hu, H., Zhu, S., Zhou, Q., Li, W., Wei, X., and Xie, K. (2005) Desulfurization of coal by pyrolysis and hydropyrolysis with addition of KOH/NaOH. *Energy & fuels*, **19(4)**, 1673–1678.

20. Nazua, N. F., Ismail, S. N. A. S., Abdullah, M. F., Ishak, M. A. M., Ismail, W. I. N. W., Ismail, K., Ahmad, R., and Abdulrrahman, M. D. (2024) Desulfurization and Optimization of High Sulfur Jambi Province Coal by Ultrasonic-Assisted Process using Peroxyacetic Acid (PAA) Treatment. *Journal of Advanced Research in Applied Sciences and Engineering Technology*, **48(2)**, 105–120.

21. ASTM D3177-89 (2022) Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke. *ASTM International, West Conshohocken, PA*, 19428-2959.

22. ASTM 2492-02 (2012) Standard Test Method for Forms of Sulfur in Coal. *ASTM International, West Conshohocken, PA*, 19428–2959.

23. Kamble, A. D., Mendhe, V. A., Chavan, P. D. and Saxena, V. K. (2022) Insights of mineral catalytic effects of high ash coal on carbon conversion in fluidized bed Co-gasification through FTIR, XRD, XRF and FE-SEM. *Renewable Energy*, **183**, 729–751.

24. Xiao, J., Wang, M., Pang, Z., Dai, L., Lu, J. and Zou, J. (2019) Simultaneous spectrophotometric determination of peracetic acid and the coexistent hydrogen peroxide using potassium iodide as the indicator. *Analytical Methods*, **11(14)**, 1930–1938.

25. Rawat, K. and Yadav, A. K. (2020) Characterization of coal and fly ash (generated) at coal based thermal power plant. *Materials Today: Proceedings*, **26**, 1406–1411.

26. Dwivedi, K. K., Shrivastav, P., Karmakar, M. K., Pramanick, A. K., and Chatterjee, P. K. (2022) A comparative study on pyrolysis characteristics of bituminous coal and low-rank coal using thermogravimetric analysis (TGA). *International Journal of Coal Preparation and Utilization*, **42(1)**, 1–11.

27. Dwivedi, K. K., Chatterjee, P. K., Karmakar, M. K. and Pramanick, A. K. (2019) Pyrolysis characteristics and kinetics of Indian low

rank coal using thermogravimetric analysis. *International Journal of Coal Science & Technology*, **6**, 102–112.

28. Xu, Y., Liu, Y., Bu, Y., Chen, M. and Wang, L. (2021) Review on the ionic liquids affecting the desulfurization of coal by chemical agents. *Journal of Cleaner Production*, **284**, 124788.

29. Mao, Y., Xia, W., Peng, Y. and Xie, G. (2019) Ultrasonic-assisted flotation of fine coal: A review. *Fuel Processing Technology*, **195**, 106150.

30. Tang, L., Long, K., Chen, S., Gui, D., He, C., Li, J. and Tao, X. (2020) Removal of thiophene sulfur model compound for coal by microwave with peroxyacetic acid. *Fuel*, **272**, 117748.

31. Yang, Y., Tao, X., Kang, X., He, H., Xu, N., Tang, L. and Luo, L. (2016) Effects of microwave/ HAc–H2O2 desulfurization on properties of Gedui high-sulfur coal. *Fuel Processing Technology*, **143**, 176–184.

32. Deb Barma, S., Baskey, P. K. and Biswal, S. K. (2018) Chemical beneficiation of high-ash indian noncoking coal by alkali leaching under low-frequency ultrasonication. *Energy & Fuels*, **32(2)**, 1309–1319.

33. Zhou, R., Luo, W., Zhu, L., Chen, F. and Tang, H. (2007) Spectrophotometric determination of carbon tetrachloride via ultrasonic oxidation of iodide accelerated by dissolved carbon tetrachloride. *Analytica Chimica Acta*, **597(2)**, 295–299.

34. Tang, Y., Chen, C., Li, X., Wei, Q., Guo, X., Finkelman, R. B., Li, W. and Huan, X. (2021) The evolution characteristics of organic sulfur structure in various Chinese high organic sulfur coals. *Energy Exploration & Exploitation*, **39(1)**, 336–353.

35. Gao, F., Jia, Z., Qin, M. L., Mu, X. G., Teng, Y. F., Li, Y. D. and Bai, Q. H. (2022) Effects of organic sulfur on oxidation spontaneous combustion characteristics of coking coal. *Energy Exploration & Exploitation*, **40(1)**, 193–205.

36. Mason, T. J. (2016) Ultrasonic cleaning: An historical perspective. *Ultrasonics sonochemistry*, **29**, 519–523.

37. Ambedkar, B., Nagarajan, R. and Jayanti, S. (2011) Investigation of high-frequency, high-intensity ultrasonics for size reduction and washing of coal in aqueous medium. *Industrial & Engineering Chemistry Research*, **50(23)**, 13210–13219.

38. Soleimani, M., Bassi, A. and Margaritis, A. (2007) Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology advances*, **25(6)**, 570–596.

39. Yang, Z. Y., Wang, S. T., Tan, C. and Li, Y. H. (2015) Desulfurization effect of high-sulfur Weibei coal of assisted by microwave irradiation and ultrasonic wave. *Advanced Materials Research*, **1070**, 501–504.

40. Albayrak, A. T. and Tavman, A. (2022) Sono-oxidative desulfurization of fuels using heterogeneous and homogeneous catalysts: A comprehensive review. *Ultrasonics Sonochemistry*, **83**, 105845.

41. Declercq, N. F., Briers, R., Degrieck, J. and Leroy, O. (2005) The history and properties of ultrasonic inhomogeneous waves. *EEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **52(5)**, 776–791.

42. Azargohar, R. and Dalai, A. K. (2005) Production of activated carbon from Luscar char: experimental and modeling studies. *Microporous and mesoporous materials*, **85(3)**, 219–225.

43. Shahraki, S., Karamoozian, M. and Azizi, A. (2018) Desulfurization of coal by HNO3 leaching: Optimization of influential factors using Box-Behnken design. *Journal of Mining and Environment*, **9(3)**, 657–665.

44. He, J., Zhu, L., Liu, C. and Bai, Q. (2019) Optimization of the oil agglomeration for high-ash content coal slime based on design and analysis of response surface methodology (RSM). *Fuel*, **254**, 115560.

45. Kong, X., Garg, S., Chen, G. and Waite, T. D. (2023) Investigation of the deactivation and regeneration of an Fe_2O_3/Al_2O_3• SiO_2 catalyst used in catalytic ozonation of coal chemical industry wastewater. *Journal of Hazardous Materials*, **451**, 131194.

46. Liu, A., Liu, S., Liu, Y., Liu, B. and Liu, T. (2022) Characterizing mechanical heterogeneity of coal at nano-to-micro scale using combined nanoindentation and FESEM-EDS. *International Journal of Coal Geology*, **261**, 104081.

47. Kumar, S. and Jain, M. K. (2022) Characterization and morphometric study of household settled dust: A case study in Dhanbad, the coal capital of India. *Applied Geochemistry*, **144**, 105398.

48. Mketo, N., Nomngongo, P. N. and Ngila, J. C. (2016) Evaluation of different microwave-

assisted dilute acid extracting reagents on simultaneous coal desulphurization and demineralization. *Fuel*, **163**, 189–195.

49. Tang, L., Chen, X. and Tao, X. (2023) Non-thermal effect of microwave on organic sulfur removal from coal by microwave with peroxyacetic acid. *Fuel*, **338**, 127262.

50. Nandiyanto, A. B. D., Oktiani, R. and Ragadhita, R. (2019) How to read and interpret FTIR spectroscope of organic material. *Indonesian Journal of Science and Technology*, **4(1)**, 97–118.

51. Wang, L., Jin, G. and Xu, Y. (2019) Desulfurization of coal using four ionic liquids with [HSO_4]. *Fuel*, **236**, 1181–1190.

52. Ismail, S. N. A. S., Ishak, M. A. M., Ismail, K., Izhan, W., Nawawi, N. N. K., Ani, A. Y., Alias, A. B. and Ahmad, R. (2022) Optimization Studies of Coal Organic Sulfur Removal using Potassium Carbonate and Ethylene Glycol as a Deep Eutectic Solvent. *Malaysian Journal of Chemistry*, **25(3)**, 97–106.

53. Cong, K., Han, F., Zhang, Y. and Li, Q. (2019) The investigation of co-combustion characteristics of tobacco stalk and low rank coal using a macro-TGA. *Fuel*, **237**, 126–132.

54. Dwivedi, K. K., Karmakar, M. K. and Chatterjee, P. K. (2020) Thermal degradation, characterization and kinetic modeling of different particle size coal through TGA. *Thermal Science and Engineering Progress*, **18**, 100523.

55. Mohalik, N. K., Mandal, S., Ray, S. K., Khan, A. M., Mishra, D. and Pandey, J. K. (2022) TGA/DSC study to characterise and classify coal seams conforming to susceptibility towards spontaneous combustion. *International Journal of Mining Science and Technology*, **32(1)**, 75–88.

56. Shen, Y., Hu, Y., Wang, M., Bao, W., Chang, L. and Xie, K. (2021) Speciation and thermal transformation of sulfur forms in high-sulfur coal and its utilization in coal-blending coking process: A review. *Chinese Journal of Chemical Engineering*, **35**, 70–82.

57. Wang, W., Lemaire, R., Bensakhria, A. and Luart, D. (2023) Thermogravimetric analysis and kinetic modeling of the co-pyrolysis of a bituminous coal and poplar wood. *Chinese Journal of Chemical Engineering*, **58**, 53–68.

58. Cao, J., Zhang, R., Shi, B., Shi, M., Zhang, L. and Liu, D. (2023) The study of co- combustion characteristics of coal and duckweed by single particle and TGA methods. *Powder Technology*, **421**, 118410.