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Desulfurization and Optimization of High Sulfur Jambi Province Coal by Ultrasonic-Assisted Process using Peroxyacetic Acid (PAA) Treatment

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ABSTRACT

The desulfurization process of high-sulfur coal from Jambi Province, Indonesia was investigated using peroxyacetic acid (PAA) as mild oxidising agent by ultrasonic wave. This study reports the utilization of a mixture of acetic acid and 6% hydrogen peroxide (CH_3COOH: H_2COOH) under sonication to extract organic sulfur from coal. The ultrasonic shockwave separates sulfur from the coal's macromolecular structure by breaking the chemical connections that hold sulfur to coal. The optimum concentration, temperature, and processing time for the coal desulfurization process were determined using the Central Composite Design-Response Surface Methodology (CCD-RSM) to overcome the traditional methods that make finding the optimal standard difficult and time-consuming. Sonicating coal at 30 ˚C for 30 minutes with 70:30 (CH_3COOH: H_2COOH) was found to be the ideal parameter. Results shows that all inorganic and some of the organic sulfur could be removed from the coal using mild conditions without severely affecting the coal microstructure as observed in the FESEM-EDX. Through the FTIR analysis, the organic sulfur structural parameters show the relative abundance of aliphatic sulfur (thiol, thiophene and sulfone) and organic matters in these coals decreased after the coal treated by PAA.To clarify its chemical effect, the production regularities of hydroxyl radical under ultrasonic field was determined using the iodine release method. Experimental results also showed that the production rule of hydroxyl radical was consistent with the desulfurization degree. These findings confirmed that the synergistic action of physical and chemical effects of the ultrasonic played an important role in this desulfurization process, which could serve as a reference for further optimizing the coal desulfurization process.

1. Introduction

Coal is a dominant fossil energy source that continues to play an essential role in various industrial applications, including power generation, steel and cement production, and the production of

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activated carbon, ceramic, silicon metal, and nanodiamond [1]. Direct combustion of high sulfur coal creates hydrogen sulfide and sulfur dioxide, gases that significantly pollute the atmosphere by forming acid rain [2,3]. Sulfur causes harm to agricultural goods, depletes the ozone layer, causes metal corrosion, which can destroy ecological buildings, and causes respiratory problems in humans and animals [4,5].

Sulfur in coal can be found mainly in pyritic, organic, and sulfate forms [6]. Organic sulfur is present in mercaptans, disulfides, thiophenes, thioethers, sulfoxides, and sulfonates, while inorganic sulfur can be found in the form of pyrite and sulfate [7,8]. During combustion, heterocyclic sulfur compounds produce sulfur oxide, while sulfate and pyritic sulfur decompose to produce inorganic oxides and SO_x. Large amounts of coal with high gross calorific value (GCV) cannot be used in thermal power plants unless high sulfur coal and SO_x pollution are controlled [6]. The most cost-effective physical method can quickly remove inorganic sulfur from coal, but it has little effect on organic sulfur [4]. Organic sulfur needs chemical desulfurization techniques due to the strength of the coal macromolecular structure [8,9].

Previous research discovered that conventional desulfurization could reduce inorganic sulfur in coal by more than 80%. Still, the removal effect of organic sulfur is insignificant, even though it destroys the macromolecular structure and properties of coal. As a result, it is essential to develop an alternative technology capable of effectively removing organic sulfur from coal [4].

Peroxyacetic acid (PAA) is a mixture of hydrogen peroxide in acetic acid that are used to desulfurize the coal. As a mild oxidizing agent for coal desulfurization, PAA is thought to produce hydroxyl cations, strong electrophiles that it reacts with sulfur because they're more nucleophilic than carbon [9,10]. The oxidation pre-treatment destabilizes the C-S bonds in the sulfur, making the sulfur component of the oxidized coal easier to thermally decompose [11,12]. PAA quickly removed pyrite, mercaptan, and thioether sulfur using microwave (MW), but heterocyclic sulfur in coal, such as the thiophene ring, remained unchanged due to structure stability [13,14]. The C-S bonds of thiophene had to be broken to remove it from coal. It has been challenging to understand the removal mechanism of the sulfur-containing bonds for thiophene in coal [13]. It is shown that the ultrasonics method has been chosen one of the main processes in coal desulfurization [8]. It is also found that the ultrasonics desulfurization was better than that of ultrasonics treatment alone. Oxidative systems, composed of peroxyacetic acid had been highly effective for sulfur removal from coal with ultrasonic waves. Combining ultrasonics irradiation and PAA treatment improved hydrophobicity, superficial area and chemical adsorption of coal and the wettability of pyrite [8].

The chemical effects of desulfurizing coal using peroxyacetic acid (PAA) were studied in Cheng *et al.,* [15]'s experiments, which examined the production regularities of the hydroxyl radical under an ultrasonics field by the iodine release technique. They discovered that the desulfurization rate and the hydroxyl radical generation rule were both accurate. According to these results, the ultrasonics' combined physical and chemical impacts were crucial to the desulfurization process. The production of hydroxyl radicals played a significant role in the desulfurization effect, which can be attributed to the oxidation removal of pyrite, mercaptan, and sulfoether, according to the study's analysis of the hydroxyl radical production law, which was determined using the iodine release method.

The investigations have made use of the valuable experimental design approach known as Design Expert. It was chosen to cut down on both the cost and the amount of time needed to complete the laboratory experiment. This program set up the experiment, analysed the data, and created the graphical depiction in addition to efficiently optimizing the procedure. This program offers a motivating array of plan alternatives and gives users a chance to pick out aspects and mix them with parameters. Once the plan is established, it generates a run chart with the tests listed randomly. Finding the relationships between various factors for parameter optimization and providing

statistical frameworks is the main objective of the novel design technique. According to several researchers, oxidising agents usually removed heterocyclic sulphur to low levels. Although the PAA was able to remove heterocyclic sulphur from coal, it was unable to specifically break the C-S bond in the thiophene ring, potentially compromising coal's inherent properties [7]. Several analytical techniques were used to examine the characteristics of coal before and after desulfurization as well as the regularity of hydroxyl radical formation in order to elucidate the combined action mechanism.

The main objective of this experiment is to study the desulfurization mechanism in the process of coal desulfurization of high-sulfur coal by ultrasonics with PAA. Moreover, this study explores optimum desulfurization conditions for sulfur removal from high-sulfur coal by utilizing PAA and found that 70:30 (acetic acid: hydrogen peroxide) was chosen to be the optimum ratio. The surface properties of samples were analyzed by FESEM-EDX to reveal the physical effect. To clarify the chemical action, the hydroxyl radical production law was determined using the iodine release method. In addition, results from FTIR analyses depicted a considerable increase in oxygen-bearing functional groups. The sonication technique uses in this study make the ultrasonic leaching shockwaves create microscopic cracks on the surface of the coal, bringing the reagent closer to the coal particles. The optimum concentration, temperature, and processing time for the coal desulfurization process were determined using the Central Composite Design-Response Surface Methodology (CCD-RSM) to minimize the number of experimental runs.

2. Methodology

2.1 Preparation of Coal Sample

SGS(Malaysia) Sdn. Bhd. provided the high-sulfur coal sample for this investigation, which came from Indonesia's Jambi Province. To achieve 212 µm particle sizes, the coal was ground into a fine powder and then sieved through progressively thinner screens. After being sieved for 30 minutes in an Endecott Shaker Model EFL2 MK3, the ground coal was dried for 24 hours at 80˚C in a vacuum oven [16]. To keep the moisture out, the coal was stored in a tightly screw-capped container. Table 1 displays the raw coal's ultimate, proximate, and forms of sulfur.

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

2.2 Chemical Desulfurization of Peroxyacetic Acid

Chemical desulphurization was carried out according to the method described by Tang *et al.,* [16] with some modifications in Figure 1 below. About 5 g of raw coal (<212µm) was dispersed in 10 ml of glacial acetic acid (99.5 % mass concentration) and 40 ml of hydrogen peroxide solution (6% mass concentration) exposed to ultrasonic energy of frequency 40 kHz according to the temperatures and times listed in Table 2. After processing, the residue solution was filtered, washed with hot distilled

water, dried in a vacuum oven at 80 ˚C for 24 hours, and conserved for further analysis. The reaction was also conducted with various acids-to-peroxide volume ratios of 20:80, 30:70, 50:50, 70:30, and 80:20.

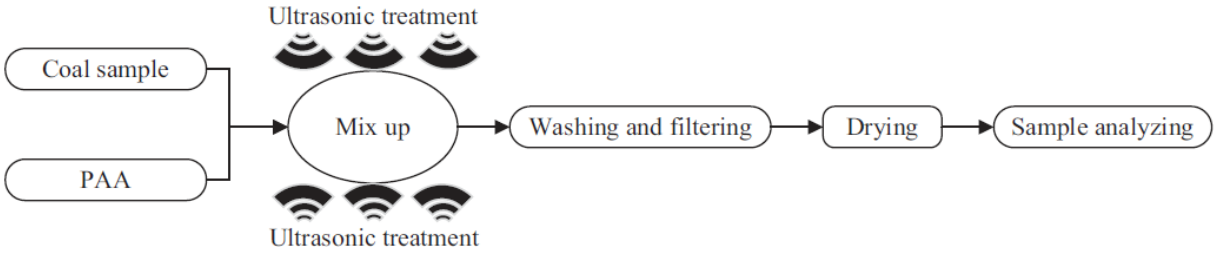


Fig. 1. The experimental procedure of coal desulfurization [16]

All the solutions were prepared and stored in sealed Schott bottles to avoid contamination and moisture. A list of the optimization parameters, including concentration, temperature, and processing time can be found in Table 2. The experiment was repeated twice to get an accurate result. Under optimum circumstances, the blank samples were created by pre-treating coal with a combination of CH_3COOH and H_2O_2 or PAA.

2.3 Sulfur Assay Studies

Total sulfur (TS) in coal was tested using ASTM D3177-02 (2012) and ASTM D2492 -02 (2012) was used to quantify sulfate sulfur (Ss) and pyrite sulfur (Ps) [17,18]. The organic sulfur (Os) was calculated by subtracting the sum of sulfate and pyritic sulfur from the total sulfur using Eq. (1), while the organic sulfur removal percentage was calculated using Eq. (2).

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

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

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

Field emission scanning electron microscopy (FESEM) is a non-destructive method used for analysing micron-sized particle size and surface characteristics [19]. The FESEM (Oxford Instrument Max 20) was used to analyse the high sulfur coal and treated coal sample under SEM-EDX to investigate the micro changes due to organic compounds' thermal cracking in coal with EDX attachment. The SEM photographs were snapped by maintaining the magnitude range between 7.00 KX to 100.00 KX. FESEM images and EDX spectra with peaks of several elements were observed after the desulfurization of coal [20].

2.5 Fourier Transform Infrared Spectroscopy (FTIR) Study

FTIR analysis was performed on raw and treated coal to determine and compare the changes in functional group absorption peaks in both samples. The sample was dried overnight at 80 ˚C before the FTIR analysis to reduce the impact of moisture. The coal samples were ground with KBr at a 1:1000 coal-to-KBr mass ratio and compressed into tiny pellets. A Perkin Elmer FTIR Spectrometer

with a scan range of 400- 4000 cm^{-1} was employed, and it was then scanned 64 times with a resolution of 4 cm^{-1} [21].

2.6 Production of Hydroxyl Radical Under Ultrasonic

The iodine release method was carried out according to the method described by Tang *et al.,* [16] to obtain the production of hydroxyl radical (·OH) under the ultrasonic field and for detecting the absorbance change of potassium iodide (KI) solution by an ultraviolet spectrophotometer (2802uv/vis) after US irradiation. The untreated aqueous solution of KI was used as a reference to ensure comparability. From Figure 2, they observed that there were two peaks (306nm and 354nm), but the peak at 354nm was broader than the other peak and its absorbance was directly proportional to the ion concentration [22]. Ion concentration referred to the concentration of iodine in the presence of potassium iodide [22]. Therefore, the absorbance at 354nm was chosen to characterize the iodine concentration.

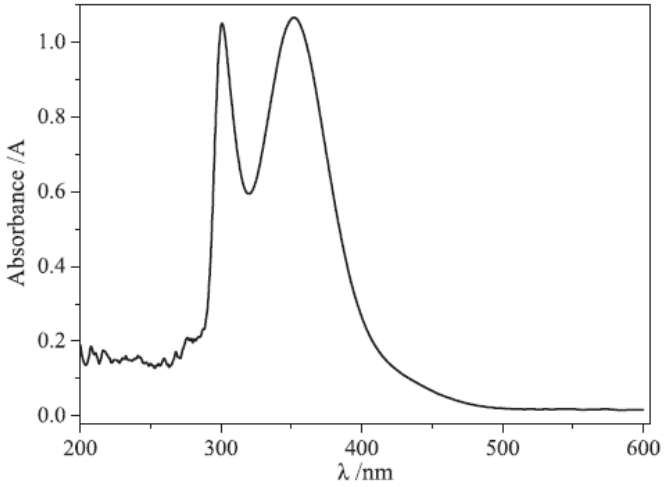


Fig. 2. The absorption spectra of KI solution after ultrasonic irradiation

2.7 Experimental Design

Three variables were selected to study their effects on the percent of organic sulfur removal from coal, including the molar ratio of PAA, temperature (˚C), and time (min). The variables denoted by the letters (A), (B), and (C), respectively, and the percent of organic sulfur removal in coal was the study's output. These parameters were optimized using Central Composite Design (CCD) under RSM in Design Expert V13, where 18 experimental runs were proposed. The studies were conducted at random to reduce response error. The parameters A, B, and C are quantitative factors that change according to the ranges listed in Table 2. The effect of the extraction parameters A, B, and C was computed using Design Expert V13. An analysis of Variance (ANOVA) is used to fit the parameters A, B, and C and the response output into a quadratic polynomial model to investigate the significance of each experimental parameter and their interactions during the desulfurization process [23]. The optimal conditions were derived from the generated response surface models.

Table 2
List of variables, codes, and design coordinates

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

3. Results and Discussion

3.1 Effect of PAA Treatments on the Microstructure of the Coal

The effect of PAA treatments on the microstructure of the coal between raw coal and optimum treated coal,70:30 (acetic acid: hydrogen peroxide) are displayed in Figure 3. The SEM micrographs for the treated coal (Figure 3(b)) indicate the appearance of hollow pits at the surface predominantly as these observation areas are probably due to the disappearance of pyrite and dissolution of some mineral matters from the surface of the coal as the results of the mild oxidizing treatment [19]. It indicates that the inorganic elements resulting from the SEM-EDX analysis and removing the carbon and oxygen to observe their differences. The SEM-EDX study revealed that raw coal was associated with less percentage of carbon content and a major amount of sulfur and oxygen-bearing and bearing less percent of silica and alumina minerals. It was found that from the EDX analysis, the sulfur content decreased in the peroxyacetic acid-treated coal because the sulfur-bearing minerals were completely soluble during desulfurization and the results are shown in Figure 4 [20]. The major content of carbon was found in optimum condition, which signified a greater amount of minerals constituents (silica and alumina) was carried out before raw coal [24].

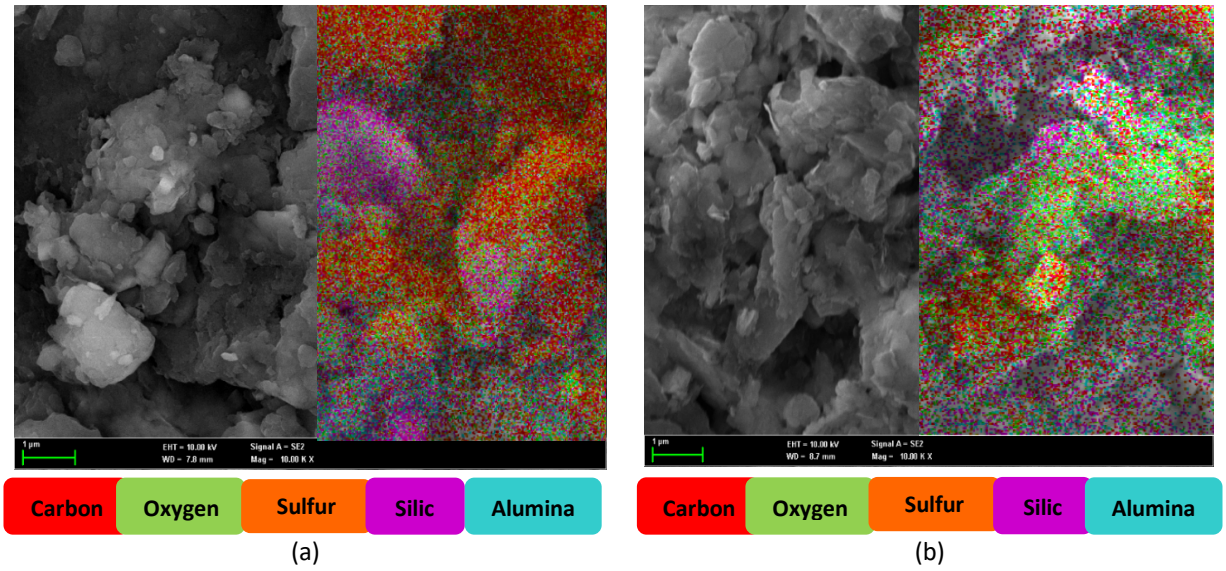


Fig. 3. SEM Image with mapping of elementary composition of (a) sulfur for raw coal and (b) treated coal at optimum condition for 30 minutes at 30°C

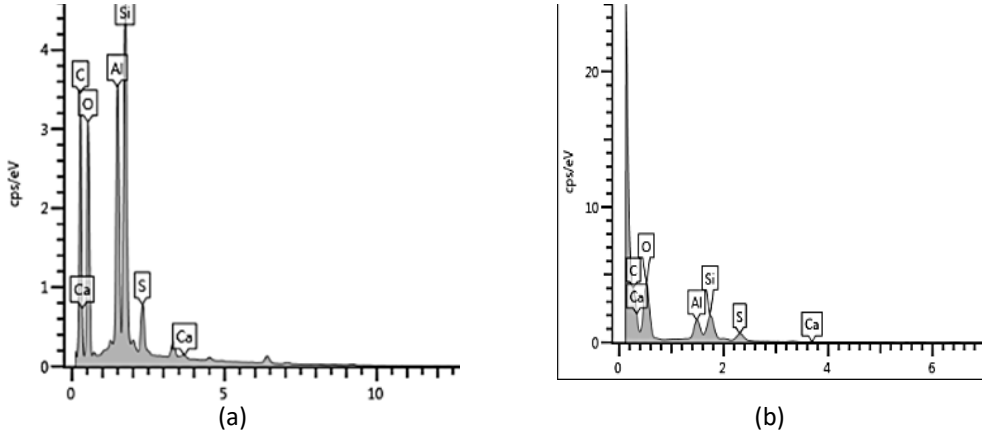


Fig. 4. EDX analysis of (a) raw coal and (b) treated coal at optimum condition at concentration ratio (70:30), for 30 minutes at 30°C

3.2 Fourier Transform Infrared Spectroscopy (FTIR) Of the Optimized Sample

Figure 5 displays the FTIR spectra of coal that has been treated with PAA and raw coal. In raw coal, thiophene rings and thiol (S-H stretch) can be identified by peaks in the 1420 cm^{-1} and 2525-2600 cm^{-1} ranges, respectively [25]. The reduction of the aromatic ring is shown by the peak at 1450–1615 cm^{-1} [26]. The presence of sulfoxide (S=O) and sulfone (O=S=O) is indicated by absorption peaks at 1330–1125 cm^{-1} and 1060–1030 cm^{-1} [27]. The stretching vibrations of the C-S and S-S disulfide bonds are shown by the peaks at 705-570 cm^{-1} and 620-600 cm^{-1}, respectively [30]. The peaks from 843-600cm^{-1} are linked to coal's inorganic and organic mineral materials indicating that the PAA quickly removed these compounds [28]. Peaks between 843-600 cm-1 correspond to the inorganic and organic mineral components in coal, showing that these compounds were rapidly eliminated during the pre-treatment process [29]. The thiophene, disulfide (C-S and S-S bonds), aromatic ring (C=C-C), and sulfoxide peaks for treated coal found to have altered and moved towards the higher wavenumber side, indicating that the mass of the molecules was lower than the peak of raw coal. As the absorption peaks of the sulfone (O=S=O), sulfoxide (S=O), and disulfide (C-S and S-S) in coal was too low and there was swamping by different oxygen-containing groups, the FTIR spectra of these compounds were too weak to identify. In conclusion, coal treated PAA may enhance the extraction of organic sulfur from coal more than raw coal.

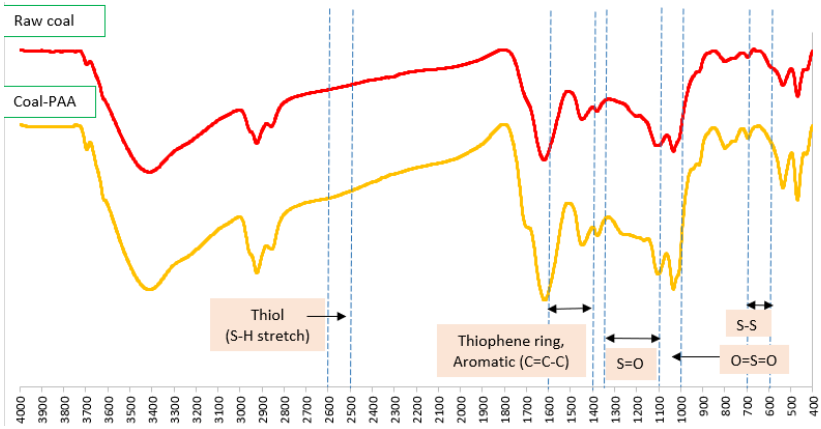


Fig. 5. FTIR results of raw coal and coal with PAA (70:30) at 30°C for 30 minutes

3.3 Model Fitting and Analysis of Variance (ANOVA)

The experimental and predicted percentages of organic sulfur removal for every 19 experimental runs conducted by CCD with various extraction parameters that show in Table 3. The appropriate quadratic model is determined by adjusting the values from the two repetition samples with a range difference of 0.2 to 0.6. Eq. (3) presents the effect of each experimental parameter and its correlation with other parameters. Negative signs show antagonistic effects and positive signs display synergistic effects [23].

$$Percent\ of\ organic\ sulfur\ removal\ (\%) = +15.45 + 2.07 * A - 6.65 * B + 2.20 * C + 2.79 * AB + 5.13 * AC - 6.38 * BC + 4.04 * A2 + 7.78 * B2 - 3.76 * C2 \quad (3)$$

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

The F-statistic test in ANOVA is used in Table 4 to ascertain the model's statistical significance [30]. Model terms' validity can be defined as probability (P) > F values [31]. If (P > F) has a value of less than 0.05, the model term is considered significant. Important terms in the model are probably going to affect the answer. By comparison, the model term becomes minor when the (P) value exceeds 0.10. With a (P > F) value of less than 0.0001, Table 4 demonstrates the significance of the selected quadratic model. The model appears to be significant based on its F-value of 2062.37. The likelihood that noise is the cause of this F-value is under 0.01%. The extraction parameters that have significance are A, B, C, AB, AC, BC, A2, B2, and C2. This is because they have a (P > F) value less than 0.05. A significant Lack of Fit describes that the model does not match the data within the range of variation seen in replicates.

Table 3
CCD experimental design with experimental and predicted percentages of organic sulfur removal

Run	Concentration (A)	Temperature (B)	Time (C)	Organic sulfur removal (%)	
				Actual value	Predicted value
1	80: 20	50	20	30.47	30.64
2	50: 50	84	20	26.56	26.63
3	70: 30	30	10	15.50	15.74
4	30: 30	70	30	2.98	2.69
5	70: 30	70	10	20.98	20.77
6	70: 30	70	30	22.65	22.66
7	30: 70	70	10	21.00	21.32
8	70: 30	30	30	43.54	43.17
9	50: 50	50	20	15.45	15.45
10	50: 50	50	20	15.88	15.45
11	50: 50	50	20	15.28	15.45
12	50: 50	50	3	1.04	0.85
13	30: 70	30	10	27.50	27.43
14	50: 50	50	37	8.07	8.33
15	50: 50	50	20	15.25	15.45
16	50: 50	50	20	15.62	15.45
17	20: 80	50	20	23.71	23.61
18	30: 70	30	30	34.18	34.34
19	50: 50	50	20	15.25	15.45

Table 4
ANOVA analysis for percentage removal of organic sulfur in coal

Source	Sum of Squares	Degree of freedom (df)	Mean Square	F-value	p-value
Model	1917.62	9	213.07	2062.37	< 0.0001[a]
A-Concentration	58.95	1	58.95	570.62	< 0.0001[a]
B-Temperature	396.2	1	396.2	3835.01	< 0.0001[a]
C-Time	66.72	1	66.72	645.78	< 0.0001[a]
AB	62.11	1	62.11	601.14	< 0.0001[a]
AC	210.64	1	210.64	2038.84	< 0.0001[a]
BC	326.02	1	326.02	3155.65	< 0.0001[a]
A^2	231.8	1	231.8	2243.66	< 0.0001[a]
B^2	521.81	1	521.81	5050.8	< 0.0001[a]
C^2	200.72	1	200.72	1942.86	< 0.0001[a]
Residual	0.9298	9	0.1033		
Lack of Fit	0.6053	4	0.1513	2.33	0.1891[b]
Pure Error	0.3245	5	0.0649		
Cor Total	1918.55	18		R^2 =	0.9995
Std. Dev.	0.3214			Adjusted R^2 =	0.999
Mean	19.52			Predicted R^2 =	0.9959
Coefficient variation (C.V. %)	1.65			Adequate Precision =	181.4734

[a]Significant value: P value less than 0.0500
[b]Insignificant value: P value greater than 0.1000

The Lack of Fit for F-values in this study is 2.33, indicating that it is insignificant compared to the pure error and this has determined an 18.91% probability of being caused by noise. This value of non-significant for Lack of Fit is good. To avoid the problem, the Predicted and Adjusted R-squared (R^2) in the data and model should be within 0.20. In this case, the Predicted R^2 (0.9959) and Adjusted R^2 (0.9990) show that the model correctly predicts the results because the difference between the two is less than 0.2. The Adequate Precision is measured by the signal-to-noise ratio. It compares the predicted value range at the design points with the average prediction error. The ratio of 181.473 shown by this study suggests an adequate signal. A ratio greater than 4 is satisfactory. This model may be used to explore the design space. Figure 6(a) displays the normal distributions of the Normal Plot of Residuals, while Figure 6(b) displays the Predicted vs Actual percent of organic sulfur removal, demonstrating that the values are still within acceptable limits.

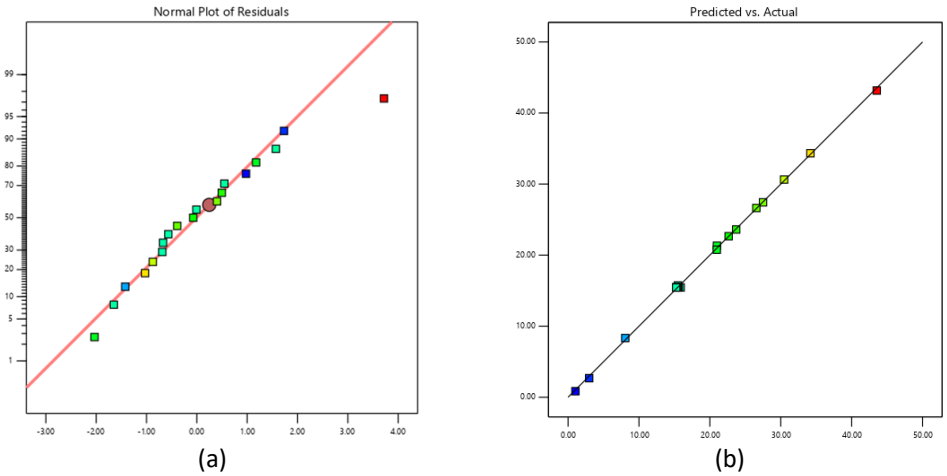
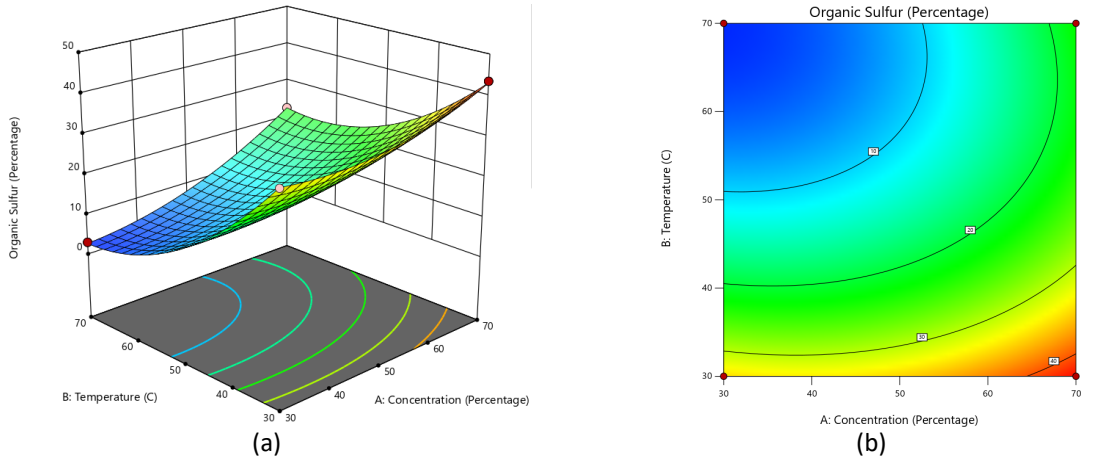


Fig. 6. (a) Normal probability plot of residuals and (b) Plot of predicted vs actual

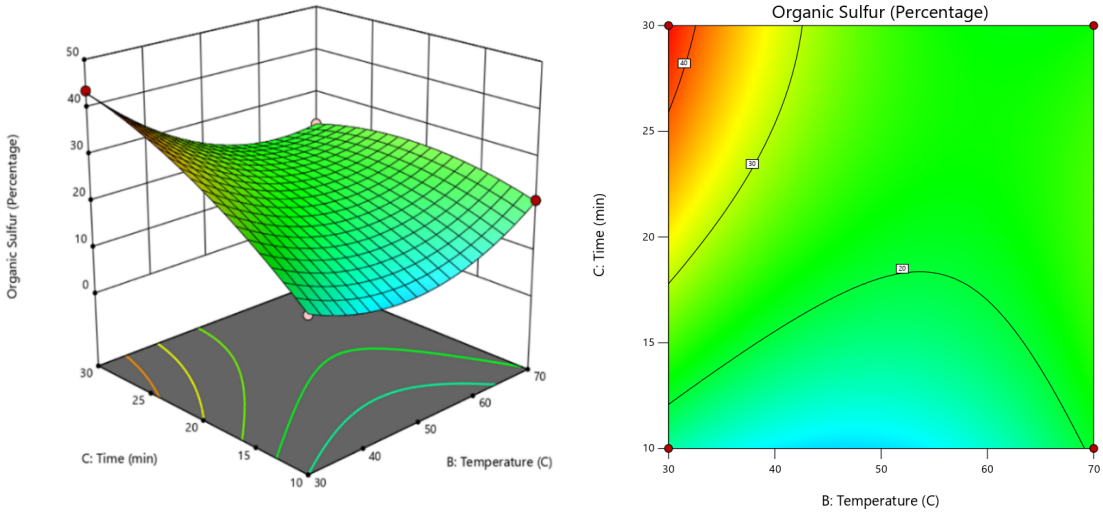
3.4 The Effects of PAA Solvents and Extraction Parameters on Coal Desulfurization

Figure 7, Figure 8, and Figure 9 display the patterns of the response surface because of changing the extraction parameters. According to the ANOVA analysis in Table 4, temperature (B) and time (C) significantly impacted the amount of organic sulfur extracted from coal due to their high F-values.



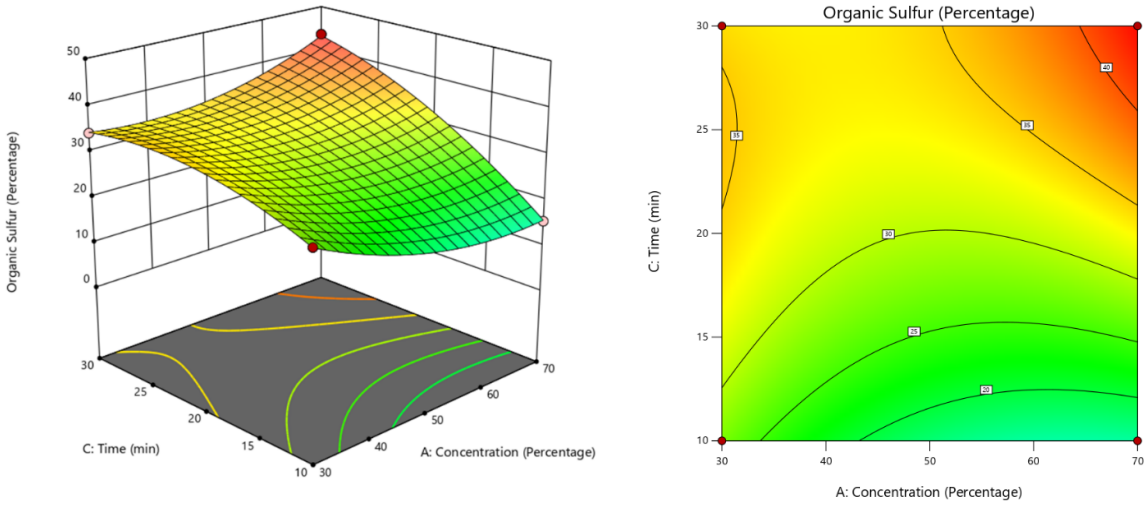
(a) (b)

Fig. 7. Effect of concentration ratio and temperature on percentage sulfur removal (a) contour plot (b) surface plot



(a) (b)

Fig. 8. Effect of temperature and time on percentage sulfur removal (a) contour plot (b) surface plot



(a) (b)

Fig. 9. Effect of concentration ratio and time on percentage sulfur removal (a) contour plot (b) surface plot

3.4.1 The effect of concentration ratio on coal desulfurization

Figure 7 and Figure 9 show the effect of the acetic acid: hydrogen peroxide (H_2O_2) ratio versus temperature and time on the desulfurization of organic sulfur coal. The highest removal of organic sulfur was 43.54%, occurring at the 70:30 ratio of acetic acid: H_2O_2 at a temperature of 30 °C for 30 minutes, while the lowest removal, 1.04%, occurred at the ratio of 50:50 of acetic acid: H_2O_2 at a temperature of 50 °C for 20 minutes. The result from Table 3 (CCD Experimental design along with experimental and predicted values of percent of organic sulfur removal) proved that the acetic acid: hydrogen peroxide (H_2O_2) ratio does not necessarily affect the removal of organic sulfur coal. The organic sulfur removal may be contributed to other factors such as temperature and processing time. It was supported by Table 4 on ANOVA analysis results which indicated that the temperature has a significant effect on organic sulfur removal since it has the highest F-value for the significant factor, followed by the processing time and the ratio of acetic acid: hydrogen peroxide. It can be deduced from the reaction between alkali and coal that the hydrogen atom in alkali can play a vital role in breaking C-S bonds and sulfur eradication [26]. Similarly, with an increase in the time processing, more time is allowed for the reaction to reach equilibrium [22].

With the concentration ratio increasing, the desulfurization amount increased first and then decreased as the concentration ratio was equal at 70:30 [31]. The maximum desulfurization degree was obtained at the ratio of 70:30 (acetic acid: hydrogen peroxide) for 30 minutes. The study by Yang *et al.,* [31] also discovered that the coal structure becomes loose, and the coal particle and pore size will expand due to the function of swelling and cavitations of ultrasonic waves. To observe the effect of ultrasonic on the production of hydroxyl radical, a 0.2 M solution of potassium iodide (KI) was treated under various reagent volume mixed ratios. Results are shown in Figure 10. When the concentration at the ratio of 80:20 of acetic acid: hydrogen peroxide (H_2O_2), the slope of this curve was the lowest as the production quantity of hydroxyl radical in the unit of time was the least. The slope of curves increases with the concentration ratio increasing, indicating that the production rate of free radical increased, until the concentration reached a maximum at the ratio of 70:30, then it decreased after achieving that concentration. All of this shows that the absorbance factor was consistent with the change regular pattern of desulfurization degree.

The effective laws of ultrasound were related to this result. Tang also stated that the cavitation

bubbles generated by the ultrasonic wave in the additives increased with the concentration, and the physical and chemical effects produced by cavitation increased which is conducive to desulfurization reaction [32]. This has resulted in many cavitation bubbles gathering around and resulting in the bubble shielding effect and reducing the conversion efficiency of ultrasound.

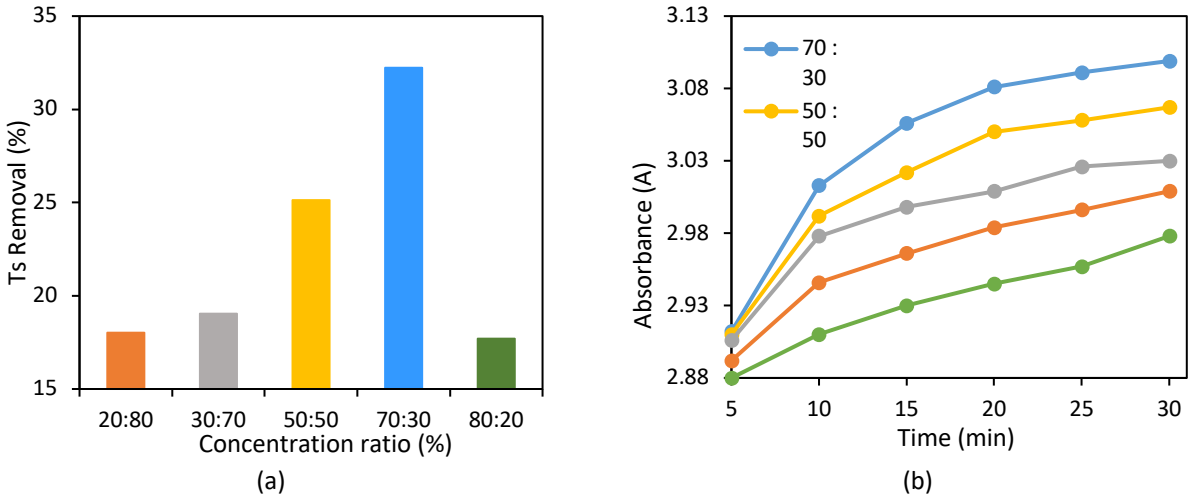


Fig. 10. Effect of ultrasonic temperature on the total sulfur removal (a) and the production of ·OH (b), temperature (30˚C), sonication time (30 min)

3.4.2 The effect of temperature on coal desulfurization

According to Figure 7 and Figure 8, when the time passed in the range of 10 to 30 minutes, the percentage of organic sulfur removed at 30˚C increased. As the temperature continued to rise from 70˚C to 84˚C, the percent elimination of organic sulfur was observed to decline. So, these findings showed that the appropriate increase of the temperature could accelerate the desulfurization reaction but low temperature for a more extended reaction period made the desulfurization process work better. The pattern is consistent with Tang *et al.,* [16] finding that the temperature rises from 30˚C to 40˚C enhanced the desulfurization degree but when the temperature exceeded 60˚C, sulfur reduction presented a slight decline [31]. According to Mao *et al.,* [12], the high-power ultrasound would increase the temperature due to the increased kinetic energy of the water molecules. This shows the possibility that the coal is thermally degraded during ultrasonic treatment. However, the acid-base complexation, an exothermic reaction, may have slowed the reaction process. Therefore, it is important to balance the amounts of sulfur removed and coal dissolved. The increase in temperature along with increasing concentration ratio enhances the reaction rate between peroxyacetic acid (PAA) present in coal.

The effect of reaction temperature on the total sulfur removal degree is shown in Figure 11. The desulfurization rate was over 24% when the temperature was in the range of 10˚C to 20 ˚C. As the temperature increased to 50 ˚C, the desulfurization effect began to decrease. The increase in temperature can intensify the decomposition of additives. To observe the effect of reaction time on hydroxyl production, the 0.2M potassium iodide (KI) mix with the PAA solution was treated by ultrasonic at different reaction times. Figure 11 shows the absorbance curves at various temperatures. The slope of the curve increases firstly with the increase of temperature and decreased as the temperature was over 30 ˚C. This study also shows that the maximum production amount of ·OH was obtained at 30 ˚C. Tang *et al.,* [16] studied that the temperature was helpful to the formation of cavitation bubbles at the beginning, but when the pressure increases inside the

cavitation bubbles enhanced the rupture of the bubble after the temperature is over 30 ˚C.

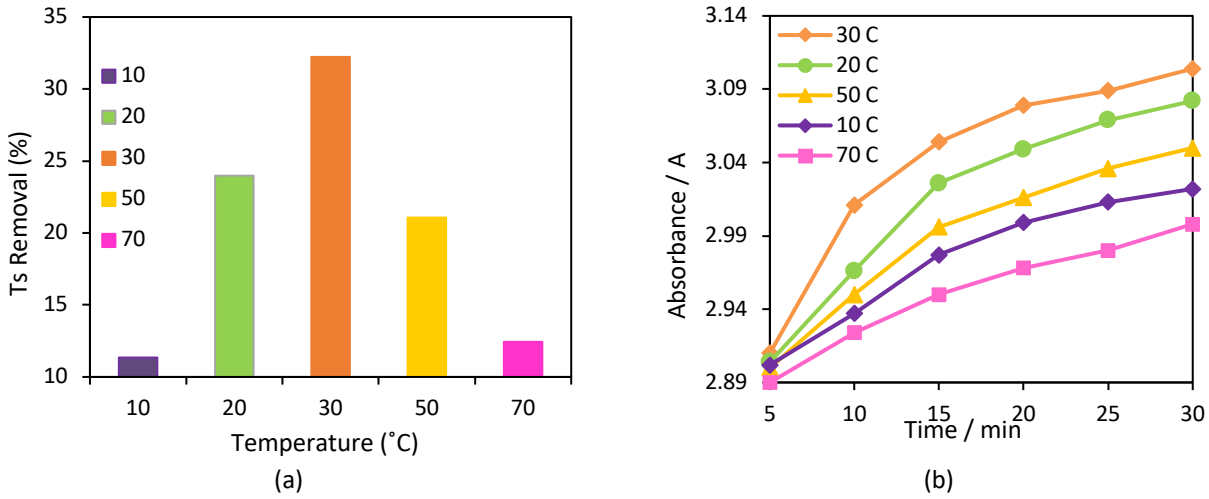


Fig. 11. Effect of ultrasonic temperature on the (a) total sulfur removal and (b) the production of ·OH, concentration ratio (70:30), sonication time (30 min)

3.4.2 The effect of time on coal desulfurization

Figure 8 and Figure 9 show the interaction of processing temperature and concentration ratio with time on the percentage of organic sulfur removal. According to the data, extending the time from 3 to 30 minutes had a consistent effect on the percentage of organic removal. The temperature and reaction time are directly proportional to the percentage of organic sulfur removed as the ANOVA analysis in Table 4 revealed. The temperature affects coal organic sulfur extraction since the temperature had the highest F-values for significant factors, followed by the time and concentration ratio. A concentration ratio of 70:30 showed the highest removal of organic sulfur after 30 minutes of reaction times.

Similar trends were seen in the effect of time on hydroxyl radical production which the increased time, the slope of the curve increase first and decreased as the time was over 30 minutes. The maximum production rate of ·OH was obtained at 30 minutes. This situation can be related to the effect of time on the total sulfur removal as shown in Figure 12. When the time was between 5 to 30 minutes, the desulfurization degree was over 32.23%. As time continue to rise, desulfurization began to decline. According to Mao *et al.,* [12], as time increases the pulp of temperature increased quickly at the first and then tended to become stable. However, the activity of the nascent oxygen, OH^- radicals, and H_2O_2 produced by ultrasonic chemical reactions is increased owing to the rising of pulp temperature, which speeds up the oxidation of the surface sulfur and causes sulfur to form sulfoxide units in the pulp.

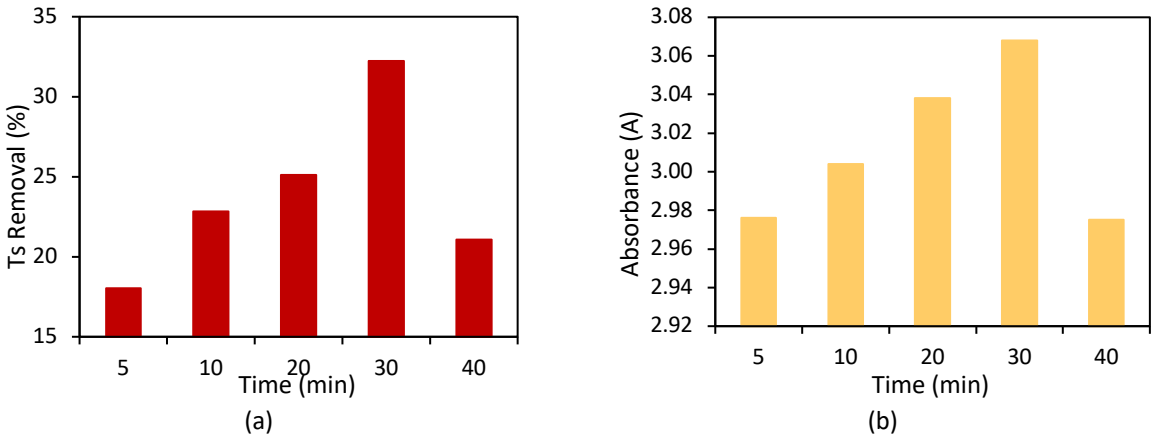


Fig. 12. Effect of ultrasonic temperature on the (a) total sulfur removal and (b) the production of ·OH, concentration (70:30), temperature (30 ˚C)

4. Conclusion and Recommendation

As for the conclusion, it was found that peroxyacetic acid (PAA) was efficient to remove the organic sulfur in the coal. The experimental results showed that all the specified concentrations (volume ratios), temperatures, and times in Table 3 could eliminate organic sulfur in coal by at least 20 to 43.54%. The optimum suggested by CCD-RSM was found at a concentration of 70:30 (volume ratio of acetic acid: hydrogen peroxide) at 30˚C for 30 minutes for processing time. However, further tests using an X-ray photoelectron spectrometer (XPS) and X-Ray diffraction analysis (XRD) are required to establish the type of organic sulfur eliminated in this research since specific organic sulfur that has a heterocyclic structure is challenging to extract from coal.

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