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Ash and sulphur removal from bitumen using column flotation technique: Experimental and response surface methodology modeling

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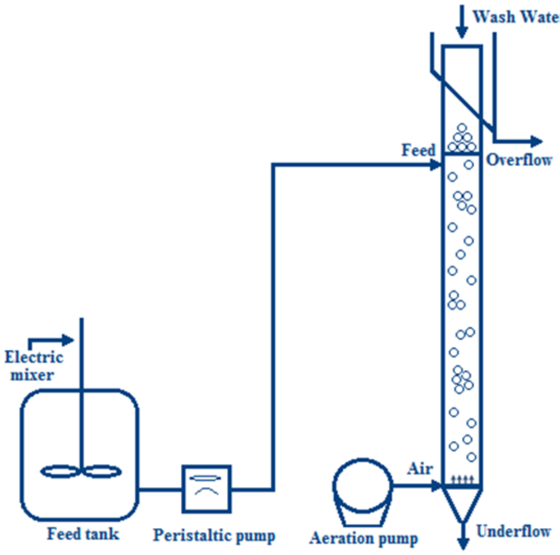
HIGHLIGHTS

- Column flotation technique is employed to remove ash and sulphur from bitumen.
- Pine oil was found as frother in this process.
- RSM is capable of optimizing the process.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates removing ash and pyrite sulphur from bitumen by column flotation process. Central composite design (CCD) of response surface methodology (RSM) was applied for modeling and optimization of the percentage of ash and pyrite sulphur removal from bitumen. The effects of five parameters namely the amounts of collector and frother agents, particle size, wash water rate and feed rate on percentage of ash and pyrite sulphur removal from bitumen were investigated. The used bitumen sample has 26.4% ash and sulphur content of 9.6% (6.81% in the pyrite sulphur form). All the tests were carried out under aeration rate of 4L/min and pulp containing 5% of solid using pine oil and kerosene as frother and collector agents, respectively. The coefficient of determination, R^2, showed that the RSM model can specify the variations with the accuracy of 0.971 and 0.975 for ash and pyrite sulphur removal from bitumen, respectively, thus ensuring a satisfactory adjustment of the model with the experimental data. The RSM was used to optimize the process conditions, which showed that initial amount of collector of 2.00 kg/$t_{bitumen}$, amount of frother of 0.2 ppm, particle size of 101.29 mesh, wash water rate of 0.5 L/min and feed rate 1.26 L/min were the best conditions. Under the optimized conditions, the maximum percentage of ash and pyrite sulphur removal from bitumen was 88.74% and 90.89%, respectively.

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1. Introduction

Bitumen is a glossy black substance consisting of different hydrocarbons with high molecular weight. Bitumen is produced by the oxidation of petroleum. Bitumen is a heterogeneous mixture of chemical compounds including about 90% of hydrocarbons, between 1% and 6% sulfur, less than 1.5% of oxygen and nitrogen molecules and a few ppm of metal components such as vanadium, nickel and iron [1]. This substance can be categorized based on various colors, hardness, density, volatile materials.

There are fertile mines of bitumen in Canada, Venezuela, Russia, Australia, and Iran. Most of Iran's bitumen can be used in solid and in the same mine form. The major mines of bitumen in Iran are located in Kermanshah, Ilam, Khuzestan provinces and other west and southwest regions. Bitumen extracted in the regions is mainly used in insulation industries, manufacture of coatings for oil and gas pipes, coking, fuel, preparation of special asphalt of road and etcetera. But, Iran bitumen has weaknesses which most importantly, is having high sulphur and mineral impurities contents. Among all the elements in the bitumen, sulphur has the most effect to limit the bitumen utilization as a clean fuel [2]. Different forms of sulphur are organic, pyrite and sulfate, which depending on the type of sulphur, there are many methods to remove them. Generally, more than half of the sulphur in bitumen is in the pyrite format [3]. Bitumen also contains inorganic minerals which are commonly called ash. The main minerals in coal are: silicates or shales (kaolinite type), quartz and sandstone, pyrite and siderite carbonates and anchorite. International standards extent the ash and sulphur value in the coal to be less than 7% and 6% respectively [4].

There are many methods for reduction of the ash and sulphur content of bitumen. Among them, the flotation techniques are widely used [5- 7]. Flotation is a separation process that depends on the difference in the surface properties of substances. Column floatation is a process utilized to selectively separate hydrophobic minerals suspended in a solution by attaching them to air bubbles and transferring them into froth layers. This is attained by using surfactants and wetting agents. It is considered the cheapest and most widely used method for separation of valuable minerals [8].

A pilot-scale flotation column was applied by Barraza and Piñeres to procreate vitrinite-rich fractions from some coal samples from Guachinte and Yolanda (south western Colombia). Maximum ash removal was obtained 71.7% and 76.5% for Guachinte and Yolanda coals respectively. Furthermore, maximum sulphur removal was acquired 63.2% and 75.4% for Guachinte and Yolanda coals respectively. In their study, Yolanda coal was afforded the highest concentration of vitrinite. It was in the order of 99.8% at neutral pH and when using the maximum frother concentration [9]. In another study, using column flotation, Piñeres and Barraza concluded that increasing of froth and aeration rate reduce coal combustible recovery [10]. Tao et al. researched flotation of a hard-to-float fine coal with a high content of ash by grinding-recleaning to roughing cleaning coal and agglomeration-floatation processes. Experimental results demonstrated that grinding-recleaning to roughing cleaning coal improved the cumulative yield from 50.87% up to 55.53% and alleviated the product ash content from 11.76% down to 10.74%. Whereas the agglomeration-floatation, the least ash of clean coal is 10.69%, with 58.72% yield, 7.85% better in yield and 1.07% lower in ash content [11]. Ashiwani et al. found that blended frothing molecules of short chain alcohol and polyglycol ether have a dramatic impact on the surface activity and flotation performance in term of ash reduction and improvement in coal yield [12]. The effect of solids pulp percentage in coal column flotation studied by Angadi et al. The impact of different variables on solids and water flow to the flotation froths are considered. They found out that increasing the concentration of frother reduces the size of the air bubbles. Also, increasing the surface area of the bubbles improve the flotation efficiency [13]. Dey et al. surveyed flotation behavior of weathered coal with a low content of ash in mechanical and column flotation cell. They found out that cleaning of the rougher concentrate is necessary to reduce its ash content, whereas the single-stage column flotation is found to be better which yields 49.6% concentrate at 12% ash [14]. Vasseghian et. al. employed flotation and leaching methods to remove ash and sulphur from bitumen by sulphuric acid. Using combination of above two methods, they succeeded to remove 47% of total sulphur and 61% of ash under optimum conditions [15].

In this study, ash and pyrite sulphur removal from bitumen was investigated in column flotation and correlated with modeling and optimization studies we used the central composite design (CCD) of response surface methodology (RSM) for analysis of operational conditions namely amount of collector, amount of frother, particle size, wash water rate and feed rate. It should be noted that using RSM to optimize and evaluation of interactive effects between variables for ash and sulphur removal from bitumen is a novel method.

2. Materials and methods

2.1. Materials and analytical tests

The bitumen samples were supplied by mines, in Kermanshah/ (Iran). Pine oil as frother was supplied by Boyakhsaz company/ (Iran) in liquid form. Kerosene as collector was purchased from the National Iranian oil products Distribution Company/ (Iran). Nitric acids with purity of 65% and hydrochloric acid (HCl) with 37% volumetric purity were provided from the Merck Company / (Germany). Desiccators (WG Dry model Box-503, Merck), Atomic absorption (GBC-932, GBC Australia) were used to prepare and analyze the sample and final product.

2.2. Experimental apparatus

The novel apparatus was designed and built to study ash and pyrite sulphur removal from bitumen. As shown schematically in Figure 1, a 10 cm- diameter flotation column of 2.5 m height made from Plexiglas material was employed in this study. A steel framework was used to keep the stability of the column. A polyethylene vessel with volume of 20 L equipped with an electric mixer was designed and used to provide initial load. Pulp feeder point was placed at 65 cm below the top of column. Pulp supplied was pumped into the column through a peristaltic pump (IP 55, WATSON-MARLOW, UK) with maximum power of 2.5 L/min. Wash water was inserted through a shower for washing foams in the column and separation of undesirable material from bubble-particle which was applied. Air was supplied through an internal sparger with 20 cm in diameter and 25 cm in height which was located at the bottom of the column. Tailings tube of the column was passed from the bottom of sparger.

2.3. Experimental procedures

The particle sizes of less than 250 µm were prepared by crushing the bitumen samples using filter. The pulp 5% was prepared using 50 g of a prepared bitumen sample (with specified characteristics). Then was washed using 500 mL water at 30 °C and decanted into a vessel. The paste mixture was rested for 1 h. The volume was reached to 1 L by adding distilled water to the vessel. This mixture was stirred for 3 min. The collector was added to the vessel and the mixture was further stirred for 3 min. The foaming agent was added and mixed for 3 min. The mixture was transported to the column through a peristaltic pump and the process was started. The flotation time was fixed at 10 min when the foam was collected on the top of the column (froth zone). The concentrate was washed with wash water with a flow rate of 0.3 L/min for 5 min to wash the hydrophilic impurities along with air bubbles. Consequently, the concentrate was dried in the oven for 1 h at 110 °C and pyrite sulphur, total sulphur and ash contents of the dried samples were determined by the method published in our previous work [15].

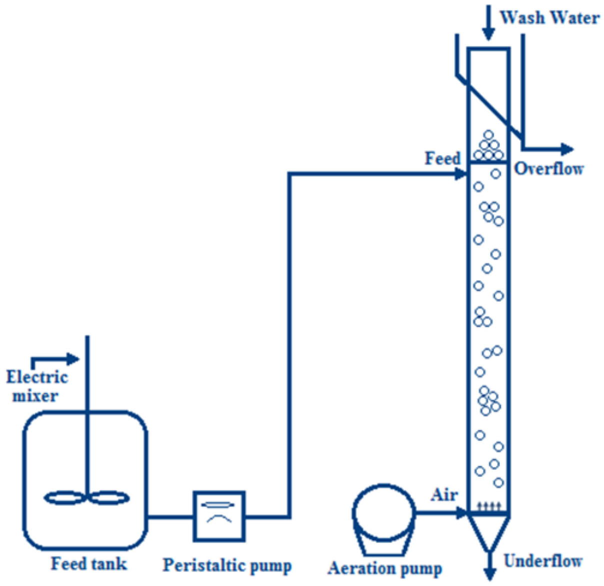

Fig. 1. A schematic illustration of the column flotation apparatus.

2.4. Response Surface Methodology (RSM)

RSM is a collection of statistical and mathematical techniques beneficial for developing, improving, and optimizing processes [16]. The most comprehensive applications of RSM are in the special situations where several input variables potentially effect some performance measure or quality characteristic of the process. So, performance measure or quality characteristic is called the response. The field of RSM includes of the experimental strategy for probing the space of the process or independent variables, empirical statistical modeling to expand an appropriate approximating relationship between the performance and the process variables, and optimization methods for finding the values of the process variables that

Table 1.

Independent variables and their levels for the central composite design used in the present study.

Independent variables	**Unit**	**Symbols**	**Level of factors**				
			- α (-2)	-1	0	1	α (2)
Amount of collector	$Kg/t_{bitumen}$	X_1	0.5	1	1.5	2	2.5
Amount of frother	ppm	X_2	0.1	0.2	0.3	0.4	0.5
Particle size	mesh	X_3	50	100	150	200	250
Wash water rate	L/min	X_4	0.2	0.3	0.4	0.5	0.6
Feed rate	L/min	X_5	0.5	1	1.5	2	2.5

produce favorable values of the response.

In this study, a central composite design (CCD) was employed in order to optimize the ash and pyrite sulphur removal. Five factors were considered: amount of collector, amount of frother, particle size, wash water rate and feed rate. Table 1 summarizes the levels for each factor involved in the design strategy. Table 2 shows the standard array for five factors and 46 experiments. It also shows the run order and the observed responses. The obtained model was evaluated for each response function and the experimental data (percentage of ash and pyrite sulphur removal) were analyzed statistically applying analysis of variance (ANOVA).

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{j<j}^{k} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (1)$$

Where y is the predicted dependent variable, β0, βj, βjj, and βij are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively, and Xi, and Xj are the independent variables. The Design expert statistical software (Design Expert 7.0.0.1, Statease, USA) was used for design of experiment, regression and graphical analyses of the obtained data, analysis of the measured responses and determining the mathematical models with best fits.

3. Results and discussion

3.1. The result of RSM model

The adequacy of the model is tested using the sequential f-test, lack-of-fit test and the analysis-of-variance (ANOVA) technique using the Design expert statistical software (Design Expert 7.0.0.1, Statease, USA) to obtain the best-fit model. In this present study, to investigate about the competency of models among various models (linear, 2FI, quadratic and cubic) to present ash and pyrite sulphur removal from bitumen, two different tests including of the sequential model sum of squares and model summary statistics were performed on the experimental data and the results are shown in Tables 3 and 4, respectively. The associated p-value of less than 0.05 for the model (i.e., α=0.05, or 95% confidence level) indicates that the model terms are statistically significant [17]. The lack-of-fit value of the model indicates non-significance, as this is desirable.

The ANOVA table for the reduced quadratic model is shown in Tables 3 and 4 for percentage of ash and pyrite sulphur removal from bitumen respectively. The reduced model results indicate that the model is significant (p-value less than 0.05). The other adequacy measures, i.e., R^2, adjusted R^2 and predicted R^2, are in reasonable agreement and are close to 1, which indicate the adequacy of the model [18]. The adequate precision compares the signal-to-noise ratio; a ratio greater than 4 is desirable [17]. The value of adequate precision ratio of 20.196 and 21.430 for ash and pyrite sulphur removal from bitumen, respectively, indicate adequate model discrimination. The lack-of-fit f-value of 1437.87 and 31.34 for ash and pyrite sulphur removal from bitumen, respectively, imply that the lack-of-fit is not significant relative to the pure error.

The final mathematical models for ash and pyrite sulphur removal from bitumen, which can be used for prediction within same design space in terms of coded factors, are given as follows:

$$\text{Ash removal (\%)} = +48.99 +6.21X_1 -10.72X_2 -1.85X_3 +0.43X_4 -0.33X_5 +1.15X_1X_2 +0.95X_1X_3 -0.026X_1X_4 -0.31X_1X_5 +0.43X_2X_3 +0.41X_2X_4 +0.80X_2X_5 -0.61X_3X_4 -0.36X_3X_5 -0.58X_4X_5 +6.28X_1^2 +5.62X_2^2 +4.88X_3^2 +4.45X_4^2 +1.17X_5^2 \quad (2)$$

Table 2.
CCD with experimental and predicted values.

Run	Type	Independent variables					Experimental (%)		RSM (%)	
		X_1	X_2	X_3	X_4	X_5	Ash removal	Pyrite sulphur removal	Ash removal	Pyrite sulphur removal
1	Factorial	2	0.2	100	0.3	1	89.81	91.73	88.41	90.54
2	Center	1.5	0.3	150	0.4	1.5	50.63	56.24	48.99	54.30
3	Factorial	2	0.2	200	0.3	1	86.91	89.37	87.66	91.10
4	Factorial	1	0.2	100	0.3	1	80.85	84.69	79.51	82.44
5	Factorial	1	0.2	200	0.3	1	76.71	80.54	74.97	79.10
6	Axial	2.5	0.3	150	0.4	1.5	82.12	86.87	86.52	89.52
7	Axial	1.5	0.1	150	0.4	1.5	89.19	90.80	92.91	93.78
8	Factorial	1	0.2	100	0.5	2	81.22	85.61	79.90	85.47
9	Factorial	2	0.2	100	0.5	2	90.40	92.52	87.46	89.32
10	Factorial	1	0.4	100	0.5	2	58.87	67.33	57.72	64.29
11	Factorial	2	0.4	100	0.5	1	69.66	72.58	69.99	73.72
12	Axial	1.5	0.3	150	0.4	0.5	51.39	55.73	54.33	57.91
13	Axial	1.5	0.3	250	0.4	1.5	61.10	68.50	64.82	70.61
14	Factorial	2	0.4	200	0.3	2	68.53	72.69	67.73	72.18
15	Factorial	2	0.2	100	0.5	1	90.74	92.80	90.77	92.68
16	Axial	0.5	0.3	150	0.4	1.5	59.22	64.60	61.68	67.43
17	Factorial	2	0.2	100	0.3	2	87.80	89.61	87.42	88.81
18	Center	1.5	0.3	150	0.4	1.5	50.60	56.18	48.99	54.30
19	Factorial	1	0.4	100	0.5	1	59.18	64.47	56.61	61.08
20	Factorial	2	0.4	100	0.3	1	70.52	73.29	65.98	69.58
21	Factorial	1	0.2	200	0.3	2	77.29	81.21	73.79	77.98
22	Factorial	1	0.2	200	0.5	1	78.22	82.09	75.02	79.72
23	Axial	1.5	0.3	150	0.6	1.5	65.01	70.49	67.65	73.39
24	Factorial	2	0.4	200	0.5	2	68.57	72.70	66.98	71.46
25	Factorial	1	0.4	100	0.3	2	58.62	62.27	55.94	60.08
26	Factorial	1	0.2	100	0.3	2	79.70	82.41	79.76	83.26
27	Center	1.5	0.3	150	0.4	1.5	50.77	55.12	48.99	54.30
28	Factorial	2	0.2	200	0.3	2	85.60	86.68	85.24	87.43
29	Factorial	2	0.2	200	0.5	1	87.80	90.02	87.60	90.00
30	Axial	1.5	0.3	50	0.4	1.5	69.10	73.51	72.24	76.88
31	Axial	1.5	0.3	150	0.2	1.5	61.71	67.69	65.93	70.27
32	Center	1.5	0.3	150	0.4	1.5	50.82	55.13	48.99	54.30
33	Factorial	2	0.4	100	0.5	2	68.47	72.41	69.86	74.39
34	Factorial	1	0.2	200	0.5	2	67.08	74.68	71.50	76.96
35	Factorial	1	0.4	100	0.3	1	51.02	53.49	52.49	55.23
36	Factorial	2	0.4	100	0.3	2	68.21	72.02	68.19	71.88
37	Factorial	1	0.4	200	0.5	1	51.33	55.71	51.37	56.19
38	Factorial	1	0.4	200	0.3	2	52.12	57.11	51.69	56.48
39	Factorial	2	0.2	200	0.5	2	86.45	87.50	82.85	84.70
40	Factorial	1	0.4	100	0.3	1	51.00	53.50	52.49	55.23
41	Axial	1.5	0.5	150	0.4	1.5	46.89	50.82	50.03	53.32
42	Factorial	2	0.4	200	0.3	1	68.80	73.19	66.96	71.82
43	Factorial	1	0.2	100	0.5	1	81.53	85.80	81.98	86.29
44	Factorial	1	0.4	200	0.5	2	52.82	57.51	51.05	57.47
45	Factorial	2	0.4	200	0.5	1	69.01	74.03	68.54	72.73
46	Axial	1.5	0.3	150	0.4	2.5	49.11	54.14	53.02	57.45

(3)

Pyrite sulphur removal (%)= $+54.30 +5.52X_1 -10.11X_2 -1.57X_3 +0.78X_4 -0.11X_5 +1.56X_1X_2 +0.97X_1X_3 -0.43X_1X_4 -0.64X_1X_5 +0.42X_2X_3 +0.5X_2X_4 +1.01X2X5 -0.81X_3X_4 -0.48X_3X_5 -0.41X_4X_5 +6.05X_1^2 +4.81X_2^2 +4.86X_3^2 +4.38X_4^2 +0.85X_5^2$

From Tables 3 and 4, it is obvious that, linear terms (X_1, X_2, X_3), interactive term (X_1X_2) and quadratic terms (X_1^2, X_2^2, X_3^2, X_4^2) have the largest effects on ash and pyrite sulphur removal form bitumen due to its higher F values as well as low p-values.

Process variables (linear, interaction and quadratic) effects in ash and pyrite sulphur removal from

Table 3.
ANOVA analysis for the percentage of ash removal from bitumen.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	p-Value	PRESS	Remarks
Adequacy of the model tested							
Linear	8.23	0.696	0.657	0.635	<0.0001	3248.65	
2FI	9.25	0.711	0.567	0.516	<0.0001	4302.08	
Quadratic	3.22	0.971	0.947	0.888	<0.0001	997.57	Suggested
Cubic	4.02	0.982	0.918	-1.312	<0.0001	20574.13	Aliased

Source	Coefficient Estimate	Sum of squares	Degree of freedom	Standard error	Mean square	F Value	p-Value
Model	48.99	8637.92	20	1.55	431.90	41.70	<0.0001
X_1	6.21	1513.75	1	0.51	1513.75	146.14	<0.0001
X_2	-10.72	4513.16	1	0.51	4513.16	435.70	<0.0001
X_3	-1.85	132.47	1	0.52	132.47	12.79	0.0015
X_4	0.43	7.32	1	0.51	7.32	0.71	0.4084
X_5	-0.33	4.20	1	0.51	4.20	0.41	0.5298
X_1X_2	1.15	41.17	1	0.58	41.17	3.97	0.0472
X_1X_3	0.95	27.38	1	0.58	27.38	2.64	0.1165
X_1X_4	-0.026	0.021	1	0.58	0.021	0.0020	0.9643
X_1X_5	-0.31	3.00	1	0.58	3.00	0.29	0.5952
X_2X_3	0.43	5.67	1	0.58	5.67	0.55	0.4662
X_2X_4	0.41	5.27	1	0.58	5.27	0.51	0.4824
X_2X_5	0.80	19.91	1	0.58	19.91	1.92	0.1778
X_3X_4	-0.61	11.21	1	0.58	11.21	1.08	0.3081
X_3X_5	-0.36	3.92	1	0.58	3.92	0.38	0.5438
X_4X_5	-0.58	10.63	1	0.58	10.63	1.03	0.3208
X_1^2	6.28	1091.59	1	0.61	1091.59	105.38	<0.0001
X_2^2	5.62	874.89	1	0.61	874.89	84.46	<0.0001
X_3^2	4.88	661.00	1	0.61	661.00	63.81	<0.0001
X_4^2	4.45	548.51	1	0.61	548.51	52.95	<0.0001
X_5^2	1.17	38.06	1	0.61	38.06	3.67	0.0667
Residual		258.96	25		10.36		
Std. Dev.	3.22						
Mean	68.53						
C.V.%*	4.70						
Adeq Precision	20.196						

*C.V.% is Coefficient of Variation.

Table 4.
ANOVA analysis for the percentage of pyrite sulphur removal from bitumen.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	p-Value	PRESS	Remarks
Adequacy of the model tested							
Linear	7.89	0.683	0.644	0.619	<0.0001	2998.78	
2FI	8.71	0.711	0.566	0.523	<0.0001	3748.83	
Quadratic	2.79	0.975	0.955	0.906	0.0021	737.77	Suggested
Cubic	3.14	0.987	0.944	-0.625	0.0008	12776.00	Aliased

Source	Coefficient Estimate	Sum of squares	Degree of freedom	Standard error	Mean square	F Value	p-Value
Model	54.30	7666.85	20	1.34	383.34	49.10	<0.0001
X_1	5.52	1197.95	1	0.45	1197.95	153.44	<0.0001
X_2	-10.11	4017.78	1	0.45	4017.78	514.61	<0.0001
X_3	-1.57	94.68	1	0.45	94.68	12.13	0.0018
X_4	0.78	23.92	1	0.45	23.92	3.06	0.0923
X_5	-0.11	0.51	1	0.45	0.51	0.066	0.8001
X_1X_2	1.56	76.29	1	0.50	76.29	9.77	0.0045
X_1X_3	0.97	28.90	1	0.51	28.90	3.70	0.0658
X_1X_4	-0.43	5.70	1	0.50	5.70	0.73	0.4012
X_1X_5	-0.64	12.68	1	0.50	12.68	1.62	0.2142
X_2X_3	0.42	5.40	1	0.51	5.40	0.69	0.4134
X_2X_4	0.50	7.87	1	0.50	7.87	1.01	0.3249
X_2X_5	1.01	31.78	1	0.50	31.78	4.07	0.0545
X_3X_4	-0.81	19.94	1	0.51	19.94	2.55	0.1226
X_3X_5	-0.48	7.16	1	0.51	7.16	0.92	0.3473
X_4X_5	-0.41	5.24	1	0.50	5.24	0.67	0.4205
X_1^2	6.05	1012.54	1	0.53	1012.54	129.69	<0.0001
X_2^2	4.81	642.11	1	0.53	642.11	82.24	<0.0001
X_3^2	4.86	655.18	1	0.53	655.18	83.92	<0.0001
X_4^2	4.38	532.53	1	0.53	532.53	68.21	<0.0001
X_5^2	0.85	19.81	1	0.53	19.81	2.54	0.1238
Residual		195.18	25		7.81		
Std. Dev.	2.79						
Mean	72.55						
C.V.%*	3.85						
Adeq Precision	21.430						

*C.V.% is Coefficient of Variation.

bitumen with respect to sum of squares (SS) of each variable obtained from ANOVA were also investigated in this study and the results are shown in Figure 2 and 3, respectively.

It can be seen from the Figures 2 and 3, that linear effect of process variables have the greatest impact (61.71%) on process, followed by quadratic and interactive effects of process variables (32.14% and 1.28%, respectively). Similarly, in pyrite sulphur removal the effects of linear, quadratic and interactive terms were 53.36, 28.63 and 2.01%, respectively. Furthermore, The residual error measures amount of variation in the response left unexplained by the model and its effect was low (4.87% and 16% for ash and pyrite sulphur removal form bitumen, respectively) in column flotation process.

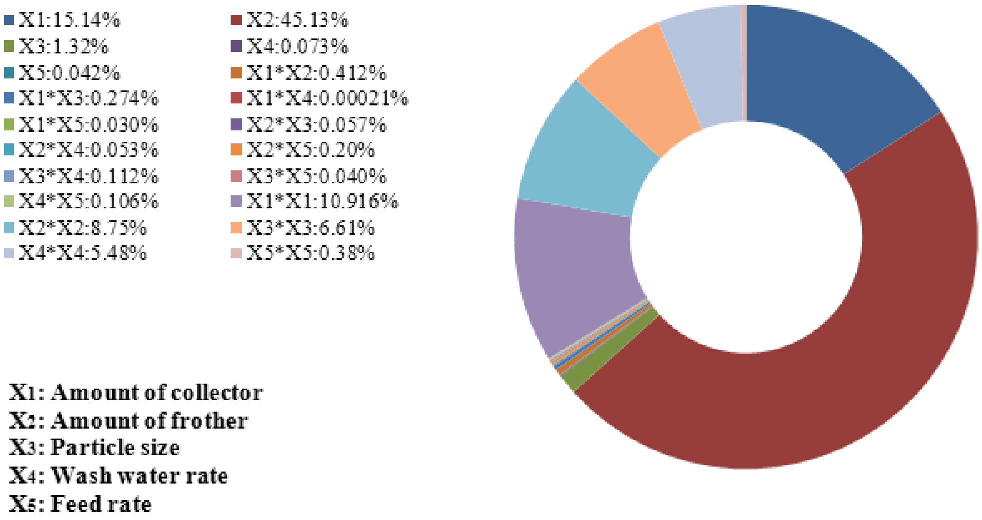

Fig. 2. Linear, interactive and quadratic effect of process variables on ash removal from bitumen.

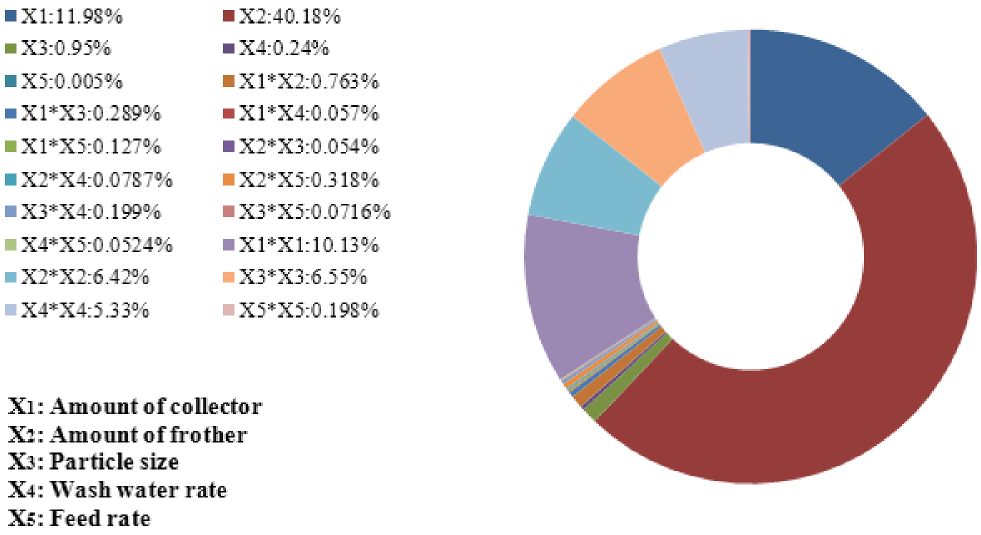

Fig. 3. Linear, interactive and quadratic effect of process variables on pyrite sulphur removal from bitumen.

3.2. Effects of process parameters on the responses

From the response surface analysis, it is clear that the variables had both positive and negative effects on ash and pyrite sulphur removal from bitumen. In order to distinguish the effects of the variables on the removal yields, 3D graphs were developed. Figures 4 and 5 illustrate the response surface plots of ash and pyrite sulphur removal from bitumen as a function of the combined positive or negative effects of significant terms in the RSM model.

3.2.1. Collector agent and ash-pyrite sulphur removal from bitumen

Figures 4-5(a-d) imply that the amount of collector has a positive effect on both the ash and pyrite sulphur removal from bitumen [19, 20]. This is because the absorption of collector on bitumen increases the hydrophobicity and consequently the floating property of particles. In the other words, the amount of pulp that goes to the froth zone increases because the contact angle of bitumen particles with water improves [13].

3.2.2. Frother agent and ash-pyrite sulphur removal from bitumen

The results show that frother agent had the most significant effect on both the ash and pyrite sulphur removal from bitumen (β2, -10.72 and -10.11 for ash removal and pyrite sulphur removal, respectively). Decreasing frother agent, the ash and pyrite sulphur removal from bitumen also increases [20] (Figure 4-5(a, e-g)). Frother rise causes the increase ash and sulphur in the froth zone because mineral matter have very little time for hydrophilic and enter the tailings part resulting stick to the bubbles and come with them to the froth zone [21]. Moreover, Interaction of hydrophilic part of pine (frother) oil and the hydrated mineral matter can cause an increase in the hydrophobicity of ash particles. This later improves the recovery process. The pine oil addition reduces the surface tension at the liquid–air interface, resulting the production of a finer bubble size distribution which improves flotation rates and recovery values. The role of frothers in flotation is to generate smaller air bubbles. The increase in frother dosage steadily increases the solid flow rate.

3.2.3. Particle size and ash-pyrite sulphur removal from bitumen

The ash and pyrite sulphur removal from bitumen declined with the rise of particle size (See Figures 4-5(b, e, h and i)), most possibly due to the lowered particle contact with air bubbles and detracted particles ability to raise bubbles to the froth zone resulting in a decrease in removal yields. Ceylan and Zeki Küçük reported that the ash and pyrite sulphur removal from bitumen can be varied as a factor of particle size [22]. The efficacious area for heat and mass transfer increases when the particle size parameter is reduced. This last causes a growth in conversion factor of pyrite to sulfate which consequently improves the sulphur removal [23]. Small particles have some benefit compared to large particles. For example flotation and recovery of small particles are much better than large particles. Also, susceptibility of small and large particles is different for each reagent. For instance, the large particles need more collectors to have the same value of hydrophobicity as those of small particles; this increases the operating costs owing to collector and frother consumption increase. In general, the flotation of large particles is feasible only in the presence of oil collectors and higher aeration rates and longer time compared to smaller particles.

3.2.4. Wash water rate and ash-pyrite sulphur removal from bitumen

The wash water rate positively affects the ash and pyrite sulphur removal, although its effect is very low. (Figure 4-5(c, f, h and j)). This can be explained by the increase in water ratio to air ratio and the large bubbles explode in the froth zone at higher wash water rate.

3.2.5. Feed rate and ash-pyrite sulphur removal from bitumen

(Figure 4-5(d, g, i and j)) presents ash and pyrite sulphur removal percentage vs. feed rate. It is obvious that feed rate has a negligible impact on reducing of the ash and sulphur percentages ($\beta2= -0.33$ for ash removal and $\beta2= -0.11$ for pyrite sulphur removal), When feed rate is increased, removal yields reduces, which this is most possibly due to an increase in suspended solids in the froth zone and turbulency in the pulp.

3.2.6. Interaction effects

As is clear from Tables 3 and 4, the only interaction between process variables for ash and pyrite sulphur removal from bitumen is X1X2 ($p\text{-value} < 0.05$). There was appreciable interaction between amount of collector and amount of frother. At low collector values, amount of frother was high when the ash and pyrite sulphur removal from bitumen touched low amount. Though, at higher collector levels, amount of frother was low when the ash and pyrite sulphur removal from bitumen achieved higher quantity (Eqs. 2 and 3). The adsorbed kerosene on bitumen emulsifies the pine oil and reduces the quantity of pine oil available for frother action [24]. The attraction between kerosene and pine oil is possible due to hydrophobic interaction. According to Aston et al. [25], low concentration of pine oil will not change the hydrophobicity that is enough to affect flotability. But when particles of varying degree of hydrophobicity are present, some high carbon content particles are likely to be depressed due to decrease in hydrophobicity and a group of high mineral matter particles are floated due to increase in the hydrophobicity.

3.3. Optimization of ash and pyrite sulphur removal from bitumen using RSM

Numerical optimization method [26] was applied to optimize the process parameters on the maximum ash and pyrite sulphur removal from bitumen using Design expert software. According to the second order polynomial equation, the optimum conditions for ash and pyritic sulphur removal from bitumen included amount of collector of 2.00kg/tbitumen, amount of frother of 0.2ppm, particle size of 101.29mesh, wash water rate of 0.5L/min and feed rate 1.26L/min. Under these conditions, the predicted ash and pyrite sulphur removal from bitumen were 88.74% and 90.89%, respectively. The optimal condition determined by the RSM optimization approach was used to confirm the

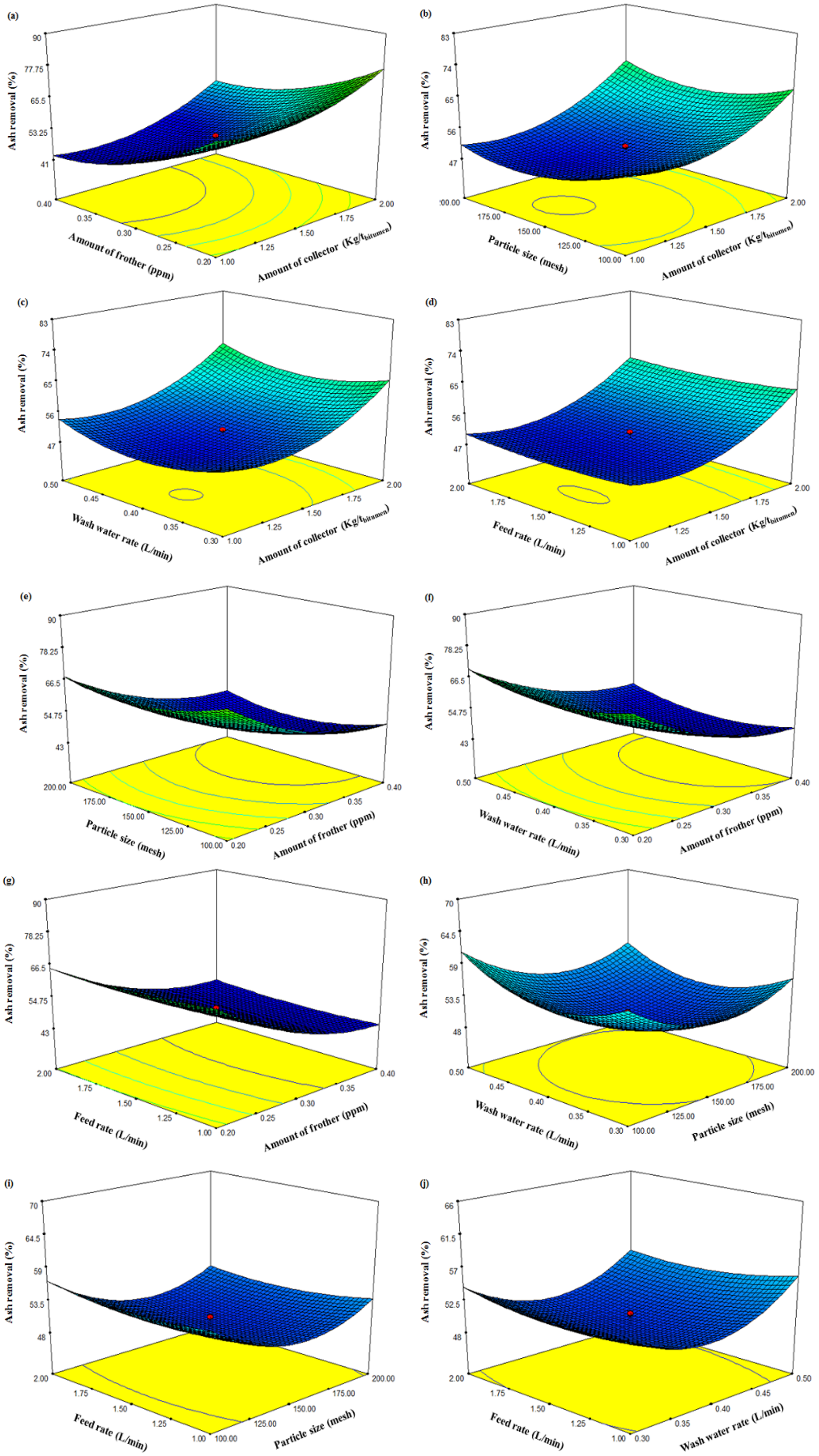

Fig. 4. Response surface plot for ash removal estimation.

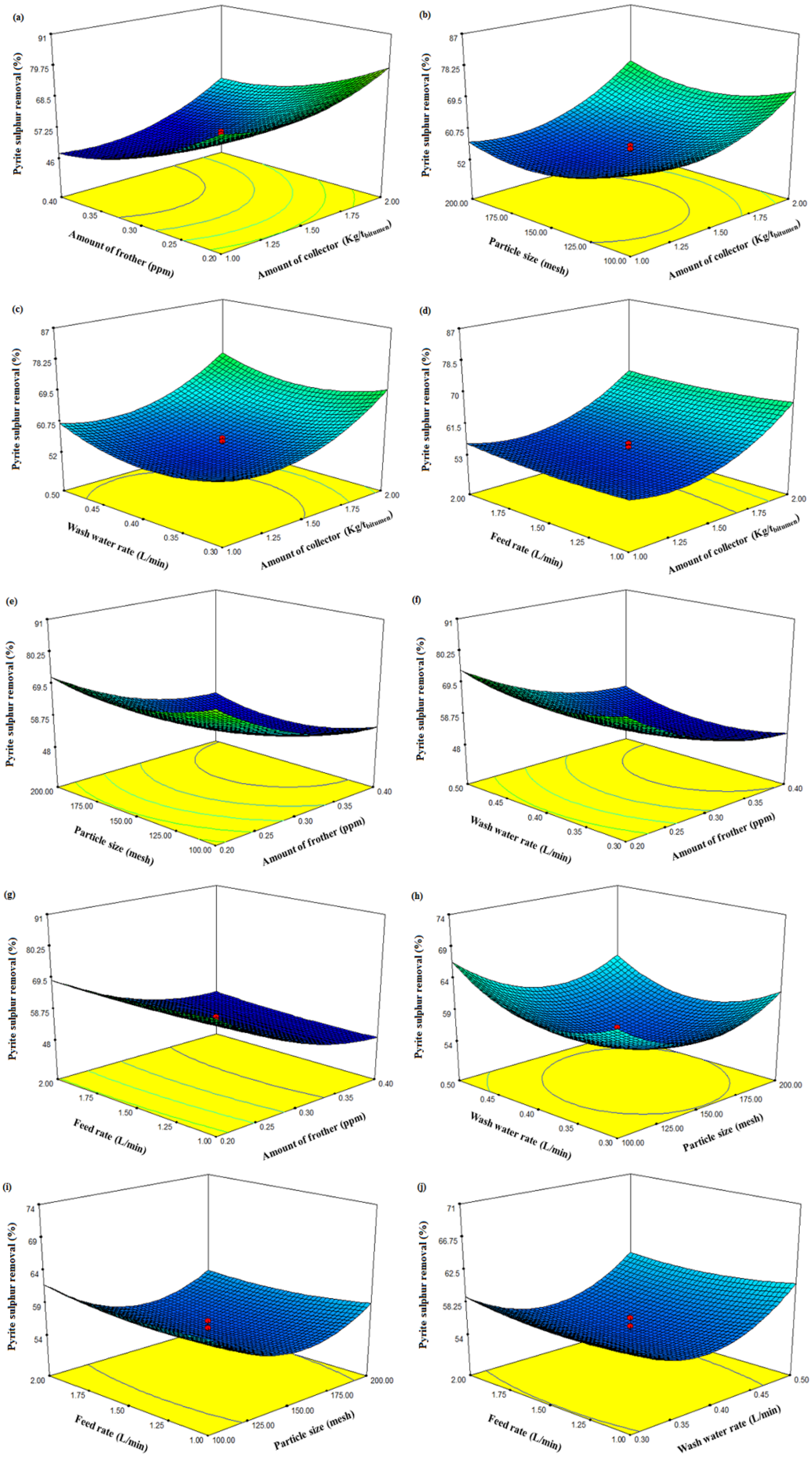

Fig. 5. Response surface plot for pyrite sulphur removal estimation.

triplicate experiments. The average ash and pyrite sulphur removal from bitumen using the triplicate experiments were 88.85± 0.21% and 90.93± 0.53%, respectively, which was very close to predicted value. For convenience purposes, the optimum conditions were slightly modified- amount of collector of 2kg/tbitumen, amount of frother of 0.2ppm, particle size of 100mesh, wash water rate of 0.5L/min, feed rate of 1L/min. The results revealed the experimental values equal to 90.74% and 92.80% for ash and pyrite sulphur removal from bitumen, respectively.

The predictability of the optimized models was investigated using five independent experimental runs. Table 5 summarized the results and demonstrated excellent confidence between the predicted and measured value.

Table 5.
The predictability of the optimized models using five independent experimental runs.

Run	Independent variables					Experimental (%)		RSM Prediction (%)	
	X_1	X_2	X_3	X_4	X_5	Ash removal	Pyrite sulphur removal	Ash removal	Pyrite sulphur removal
1	1	0.4	200	0.4	1	46.01	50.29	46.05	50.47
2	1	0.2	200	0.4	1	72.78	76.79	70.55	75.02
3	1.5	0.2	150	0.3	1.5	71.82	74.49	69.76	73.33
4	1.5	0.3	150	0.3	1.5	55.20	59.27	53.01	57.90
5	2	0.4	200	0.4	1	63.98	69.21	63.30	67.88

4. Conclusions

Column flotation process was employed for ash and pyrite sulphur removal from natural bitumen extracted from Kermanshah mines. A bitumen sample was used with sulphur content of 9.6% (6.81% in the pyrite sulphur form) and 26.4% ash. All the experiments were performed with aeration rate of 4L/min and pulp containing 5% of solid using kerosene and pine oil as collector and frother, respectively. The results indicate that the amount of collector influenced the ash and pyrite sulphur removal from bitumen. Moreover, the second factor i.e. the ash and pyrite sulphur removal from bitumen decreases with the increase of amount of frother. It was observed that the particle size and feed rate has an opposite effect on ash and pyrite sulphur removal from bitumen. Whereas, wash water rate has positive effect on ash and pyrite sulphur removal from bitumen. It should be noted that the effect of two recent variables namely wash water rate and feed rate on ash and pyrite sulphur removal from bitumen are negligible.

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