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Design of experiments to optimize the extraction parameters of a power grade Indian coal

Heena Dhawan[1] · Sreedevi Upadhyayula[2] · D. K. Sharma[1]

Abstract Low grade high ash coals with difficult physical washability characteristics require chemical cleaning techniques such as solvent extraction to obtain super clean coal with lower ash contents. Kedla, an Indian low grade coal has ash content around 44%–50% and there is a need to maximize its solvent extraction yield so as to make this power grade coal industrially useful. This paper highlights the use of definitive screening design and response surface methodology to extract the maximum organic matter from Kedla coal using ethylenediammine (EDA) and N-methyl pyrollidone (NMP) as solvents under mild atmospheric pressure conditions. The coal was pre-treated with acetic acid before extractions were carried out. The parameters such as the acid pre-treatment time, acid concentration, particle size, the co-solvent concentration and the solvent concentration were optimized in this paper. With this design of experiments technique about 40% of the organic matter with minimal ash (less than 2%) content was rendered extractable unlike the already postulated designer solvent system—e, N system (i.e. NMP containing small amount of EDA) that uses coal to solvent ratio as 1:17 (wt/vol) and coal to co-solvent ratio as 1:1(wt/vol) thus only giving 19% extraction yield. Therefore, the present design of experiments technique helps in conserving the number of experiments for process intensification.

Keywords Coal · Extraction yield · Acid pre-treatment · Definitive screening design · Response surface methodology

1 Introduction

Coal is one of the most widely used fuels. It is used both as a fuel for generation of electricity and as a non- fuel for the production of value added chemicals and products (Song and Schobert 1993, 1996; Nyathi et al. 2013). Coal is also the biggest contributor to the pollution in the world. With the limitations being imposed on the CO_2, NO_2 and other harmful gases emissions into the atmosphere, it becomes all the more important to have cleaner coal combustion and utilization. Coal is basically a condensed macro-molecular polymeric structure (Krevelen 1993; Larsen et al. 1985; Hall and Larsen 1993; Chen et al. 1998). Most of its structural constituents are aromatics, paraffinics, heteroaromatics and hydroaromatics which are held by various covalent and non-covalent interactions. These interactions are vanderwaal interactions, aromatic-aromatic, charge transfer and donor acceptor interactions between the aromatics and heterocyclic units (Haenel 1992; Nishioka and Larsen 1990; Larsen and Mohammadi 1990; Otake and Suuberg 1997; Painter et al. 1990; Rahman et al. 2017).

Indian coals are of the drift origin and the mineral matter is finely dispersed in the organic matter of these coals (Kumar and Patel 2008; Sharma and Giri 2016). High ash contents also lead to the increase in the transportation cost of coals, reduced calorific values and also results in slagging and fouling of the boilers, turbines, gasifiers etc. Therefore, it becomes important both economically and environmentally to reduce the ash contents in these coals.

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Ash content varies from 20% to 55% in Indian coals but their sulphur contents are comparatively lower ($< 0.6\%$) (Mishra 2009). There are various methods to reduce the ash present in coals- physical, chemical and biological. However, physical techniques use less expensive resources such as water, air pulsations etc. Chemical treatments such as organo-refining and chemical leaching give better extractability of coals with much reduced ash contents (Balakrishnan et al. 2015; Meshram et al. 2015). Biological treatments use microbes to digest the mineral matter in coals (Jain and Sharma 2004). The effectiveness of each method depends upon the degree of dispersion of ash in the organic matter of coals.

Coal consists of two components—organic matter (carbonaceous matrix) and inorganic matter (mineral matter). Organic matter can be extracted using solvent extraction which leaves behind solvent refined clean coal product which has negligible ash contents (Kihong et al. 2016). The role of the solvent is to break the coal–coal interactions and replace it with the coal solvent interactions. Coal being a heterogeneous polymer shows a tendency to swell in organic solvents (Takanohashi and Iino 1995; Hernández et al. 2012; Hu et al. 1998; Mathews et al. 2015). Some solvents that have the characteristic property of donating a pair of electrons show good swelling. Mostly N and O donors are considered to be good solvents for coal extraction. Swelling gives a good idea of the extent of coal interaction with the solvent that may not necessarily always account for good extraction e.g. ethylenediamine (EDA) (Krevelen 1993). Early studies on coal extraction include the use of some basic solvents such as benzene, $CHCl_3$, alcohol, ether, carbon disulphide as reported by Van Krevalan (1993). Coal derived solvents are also used for extraction. Coal tar and coal tar pitch were used by Honda et al. Higher boiling fractions like anthracene oils gave better extraction yields (Mishra and Sharma 1990; Elliott 1981). About 95% extraction yield has been reported by Orchin et al. with the use of boiling phenanthrene as a solvent (Krevelen 1993).

N-methyl pyrrolidone (NMP) is considered to be a good solvent for coal extraction (Renganathan and Zondlo 1993; Takanohashi et al. 1996; Kirk and Othmer 2006; Dryden 1948). It is an H-bond acceptor and has good interacting ability with the aromatic structures. It is used as a solvent in oil refineries for the separation of olefins and aromatics. Renganathan and Zondlo have reported as high as 50% extraction yields with NMP under atmospheric pressure conditions (Renganathan and Zondlo 1993; Renganathan et al. 1988). EDA has the ability to interact with the coal structure most powerfully by disrupting the −OH bonds. It is considered to be a good swelling solvent (Shibaoka et al. 1979; Suuberg et al. 1994; Kwak 2005).

Response surface methodology (RSM) is an analytical technique used for solving several scientific problems with minimal experimentation (Chandaliya et al. 2012). The purpose behind using this technique is to maximize the dependent output variable (response) based on the different independent input variables. A number of parameters rule a particular reaction and this methodology gives an optimum outcome of response surface corresponding to a certain reaction for maximum desirability of a particular product (Li et al. 2004; Kincl et al. 2005; Aslan and Cebeci 2007; Gunaraj and Murugan 1999; Azimi et al. 2013; Segurola et al. 1999). If y is the response corresponding to the x set of variables that govern the reaction, the relationship could be expressed as shown in Eq. (1),

$$Y = f(x_1 \times x_2 \times x_3 \times \ldots x_m) \tag{1}$$

The parameters or the factors for a reaction could be continuous, i.e. the ones that continuously affect the course of a reaction or categorical, that do not continuously affect the course of a reaction and generally this expression is expressed in the form of a second order equation as shown in Eq. (2),

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} x_i x_j + £ \tag{2}$$

where x stands for the variables that are the input parameters of the reaction and the β for the unknown coefficients and $£$ is the error. The β values are calculated using the second order model. The software using these equations gives a minimum number of experiments to be performed in order to get the desired output.

The present paper highlights the use of definitive screening design (DSD) and response surface methodology (RSM) in order to maximize the extraction yield of an Indian Coal, Kedla. It involves a two step process, pre-treatment with acetic-acid followed by extraction with NMP containing a small amount of EDA (co-solvent). Being a high ash coal, pre-treatment with acid enhances the extraction yield as the acid loosens the coal structure and breaks important linkages in coal making the inroads of the solvent easier inside the intermolecular spaces in coal (Masaki et al. 2005; Li et al. 2004). The work on the development of designer solvent e, N where coal: NMP ratio is taken as 1:17 (wt/vol) and coal:EDA ratio taken as 1:1 (wt/vol) has already been studied before in author's laboratory (Pande and Sharma 2002; Iino et al. 1988). However, presently the optimization of acid pre-treatment conditions followed by solvent extraction using design of experiments has not been reported before. Parameters taken for the study in the present paper are coal particle size, pre-treatment of coal with acetic acid by varying the coal to acid ratio, acid pre-treatment time, coal to solvent ratio, % of co-solvent in the solvent. The solvent extraction time has been optimized separately.

2 Materials and methods

2.1 Coal sample and the solvents

Kedla coal, an Indian non-coking power grade coal was procured from NTPC (National Thermal Power Corporation), New Delhi. The proximate and ultimate analysis was performed according to IS 1350 standards. The ultimate and proximate analysis of the coal sample and the properties of the solvents used are presented in Tables 1 and 2. The acetic acid from Fischer Scientific, N-methyl pyrrolidone (NMP) from SRL and ethylenediamine (EDA) from LOBA chemicals were used for present extraction studies.

Equations used for the calculations:

On clean coal product basis:

Extraction yield (% daf basis)

$$: \frac{weight(clean\ coal)}{1 - \frac{ash\%}{100} \times weight(clean\ coal)} \times 100\%$$

On loss in weight basis:

Extraction yield (% daf basis)

$$: \frac{initial\ weight(raw\ coal) - weight(clean\ coal)(100 - ash\%)}{1 - \frac{ash\%}{100} \times weight(clean\ coal)}$$
$$\times 100\%$$

Daf: dry ash free basis

2.2 Design of experiment (DOE)

The experiment was designed based on three levels—low, medium and high level factorial design with the variation of five main factors—the coal particle size, pre-treatment time of coal with acid, coal/acid (wt/vol) ratio, co-solvent concentration and the solvent concentration (Tables 3, 4).

Then based upon the results for those five parameters, a three level factorial design using RSM methodology was used for further optimization (Tables 5, 6).

Particle size is one of the most important parameters for coal extraction studies as coal extraction largely depends on the lump size that is fed into the reactors. Lesser the particle size better is the interaction of coal with the solvents which ultimately affects the extraction yields. Therefore, the upper limit for particle size was chosen as + 250 μm and lower limit as − 125 μm for the present study. The coal to acid (wt/vol) ratio was taken as 1:10–1:20. This range was of coal amount was found to be suitable for the effective interaction and pre-treatment with acetic acid. Moreover, the acid recovered after filtration can be reused. The time of acid pre-treatment was taken from 30 min (low level) to 120 min (high level) as after the pre-treatment with the acetic acid, extraction for 2 h with the solvents (NMP and EDA) was performed. The coal to solvent ratio was kept between 1:10 and 1:20 as in between these limits, the fluidity of the coal–solvent mixture is maintained. Also with excessive use of solvents, their recovery becomes difficult and the process becomes more uneconomical. 10%–15% of co-solvent EDA of total solvent concentration (vol/vol) was found enough to effectively break important linkages such as H-bonds in coal in order to make inroads for the main solvent NMP into the condensed coal structure (Pande and Sharma 2002).

Another important parameter that was optimized separately was the time of the solvent (NMP–EDA) extraction. It was kept for 2 h for each run and was optimized separately, which has been explained later in the text. Based on the responses of the definitive screening design, a three level continuous factor based RSM experimental design was developed as presented in Table 6.

2.3 Experimental procedure

For each run of the DSD experiment, Kedla coal (2 g) was taken in a 250 mL round bottomed flask along with the acetic acid and refluxed for the desired time as shown in Tables 3 and 4. The solution was then filtered and the coal dried overnight in oven at 105°C. This coal was used for refluxing in a 250 mL round bottomed flask under milder ambient pressure conditions with the given concentration

Table 1 Proximate and ultimate analysis (wt%) (on air dried basis) of Kedla coal

Proximate analysis			Ultimate analysis (daf)					Calorific value (cal/g)
M_{ad}	A_d	VM_{daf}	C	H	N	S	O^a	
0.99	44.86	17.18	52.9	3.3	1.1	0.5	42.2	4209

[a]By difference

Table 2 Properties of the two main solvents, NMP and EDA

Solvent	T_b (°C)	ρ (20 °C)	η (N/m^2)	μ (D)	DN	δ (jcm^{-3})$^{1/2}$
N-methyl pyrrolidone	202	1.028	1.67	4.09	27.3	22.9
Ethylenediamine	118	0.903	1.54	1.99	55.0	25.3

T_b, boiling point; ρ, specific gravity; η, viscosity; μ, dipole moment; DN, donor number; δ, solubility parameter

Table 3 Three level factorial design for optimization of five parameters

Levels	Particle size (μm)	Time of acid pre-treatment (min)	Coal/acid ratio(wt/vol)	% Co-solvent (EDA) in solvent (vol%)	Coal/solvent (NMP) ratio (wt/vol)
Low level (− 1)	− 125	30	1:10	10	1:10
Average (0)	125–250	60	1:15	12.5	1:15
High level (1)	+ 250	120	1:20	15	1:20

Table 4 13 Run definitive screening design (DSD) for optimization of five parameters

Run no.	Particle size (μm)	Time of pre-treatment (min)	Coal/acid ratio (wt/vol)	% Co-solvent (EDA) in solvent (NMP + EDA) (vol%)	Coal/solvent (NMP) ratio (wt/vol)	Response (Y) (extraction yield %)
1	1	0	− 1	1	1	23.18
2	1	− 1	0	− 1	1	19.01
3	− 1	− 1	− 1	1	0	27.28
4	− 1	− 1	1	0	1	37.95
5	1	1	1	− 1	0	22.74
6	− 1	1	− 1	− 1	1	30.56
7	1	− 1	1	1	− 1	18.25
8	0	1	1	1	1	27.63
9	− 1	1	0	1	− 1	18.35
10	1	1	− 1	0	− 1	23.66
11	− 1	0	1	− 1	− 1	34.73
12	0	0	0	0	0	12.54
13	0	− 1	− 1	− 1	− 1	28.02

Table 5 Three levels for the factorial design (for RSM methodology—further optimization of extraction parameters)

Item	Particle size (μm)	% Co-solvent (EDA) in solvent (NMP + EDA) (vol%)	Coal/solvent (NMP) ratio (wt/vol)
Low level (− 1)	− 125	10	1:10
Average (0)	125–250	12.5	1:15
High level (1)	+ 250	15	1:20

in Table 4 of the solvent—NMP and co-solvent EDA for 2 h. The coal solvent mixture was cooled and then filtered. The filtrate was distilled-off to remove the excess solvent and the clean coal product was precipitated using water as the anti-solvent. The recovered solvent can be reused. The residual coal and the clean coal product were washed with 2%–5% aq. HCl solution and water. Both were then dried overnight in an oven at 100 °C and weighed to obtain the extraction yield.

For each run of the RSM experiment, the coal sample (2 g) of the particle size, as mentioned in Table 6, was taken in a round bottomed flask and refluxed for about an hour with 30 mL (Based on DSD responses) of acetic acid (Li et al. 2004). The coal–acid mixture was cooled and filtered. The acid treated coal was then dried overnight in an oven at about 100 °C and weighed. This was then refluxed under milder ambient pressure conditions with the amount of the co-solvent (EDA) and the solvent (NMP) as

shown in Table 6 for about 2 h. Following the same procedure as already mentioned, the extraction yield was calculated both on clean coal product basis and on loss in weight basis.

3 Results and discussion

3.1 Extraction time

In each run, the solvent (NMP–EDA) extraction time has been taken as 2 h. Another set of experiments with the variation in the experimental time and keeping the coal to EDA (1:1) (wt/vol) and coal to solvent (1:17) (wt/vol) ratio fixed were carried out. The graph obtained for the extraction yield (%) versus time (h) has been shown in Fig. 1.

About 26.2% of the extraction yield could be obtained in just first 2 h of extraction which is about 60% of the total

Table 6 15 Runs experimental set up obtained using response surface methodology-Box Behnken design

S. no.	Particle size	% Co-solvent (A) in solvent (A + B)	Coal/solvent (A + B) ratio	Experimental value–particle size (μm)	Experimental value–co-solvent (mL) (for 2 g coal)	Experimental value–solvent (mL) (for 2 g coal)
1	0	− 1	− 1	125–250	3.75	26.25
2	1	− 1	0	− 125	3	27
3	1	1	0	125–250	3	17
4	0	− 1	1	125–250	6	34
5	1	0	− 1	125–250	2	18
6	0	1	1	+ 250	5	35
7	− 1	0	1	− 125	4.5	25.5
8	0	0	0	+ 250	2.5	17.5
9	1	0	1	− 125	2.5	17.5
10	0	0	0	+ 250	4.5	25.5
11	0	1	− 1	125–250	4	36
12	− 1	− 1	0	125–250	3.75	26.25
13	− 1	0	− 1	+ 250	3	27
14	0	0	0	125–250	3.75	26.25
15	− 1	1	0	− 125	5	35

possible exhaustive extraction yield of 45% (obtained in 24 h). Therefore, keeping in mind, the added extra consumption of resources (electricity, equipment etc.) and avoiding much complexity in extraction conditions, the appropriate extraction time in each NMP–EDA run was taken as 2 h.

3.2 Screening and interpretation of data

Minitab(18) and JMP(11.0) were used to generate the runs and for the interpretation of the responses. The screening for the DSD for the optimization of five parameters gave relevant input that the significance of particle size, % co-solvent concentration and the coal/solvent concentration was much more than the other two parameters (acid pre-treatment time and coal to acid ratio) for the extraction. Their extent of influence was measured by their p-values
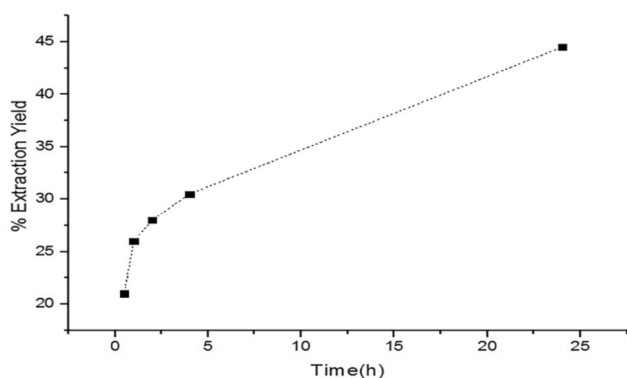

Fig. 1 A plot of extraction yield (%) versus time to optimize the extraction time of Kedla Coal

and t-ratios. The particle size shows a larger negative t-ratio value followed by the % co-solvent and then a positive t-ratio for the solvent concentration (Fig. 2). The effect of acetic acid pre-treatment and time of acid pre-treatment were not found to be as high as compared to the other parameters because acetic acid selectively acts on Ca and Mg cations in coal that are bridged through oxygen functional groups especially in low-rank coals (Masaki et al. 2005; Li et al. 2004). Its selectivity to act upon the certain cations in coal makes it relatively less significant to drastically influence the extraction yields. Moreover, NMP acts upon aromatic rings and breaks the strong cross-linkages in the coal macromolecular structure and EDA cleaves H-bonds in coals thereby promoting the action of the main solvent NMP (Pande and Sharma 2002). The particle size provides more surface area for the action of these solvents. Thus these three parameters—particle size, % co-solvent (EDA) concentration and the coal/solvent (NMP) concentration were used again for response surface methodology (RSM) in order to further maximize the extractability.

The responses (extraction yields) on clean coal product basis were found to be in good agreement with the loss in weight basis with a standard error of about 2%–3%. Using JMP (11.0), the effect of the three scaled down parameters-particle size, % co-solvent in solvent (A/A + B) and coal/solvent (Coal/A + B) ratio were studied (Table 7). The responses well fitted with the second order equation obtained with the RSM-Box Behnken method and the R^2 value (ratio of the sum of squares of the predicted responses to the sum of squares of the observed responses) was also found to be 0.966 (Table 8) which verified the good strength of model fitting. Final experimental

Term	Contrast	Plot of t-ratio	Length t-ratio	Individual p value	Value
Particle size	− 3.68627		− 1.93	0.0731	0.4614
%A in solvent	− 1.78657		− 0.94	0.3238	0.9950
Coal/(A + B)	1.34365		0.71	0.4707	1.0000
Coal/acid	0.75427		0.40	0.7251	1.0000
Time of pre-treatment	− 0.66393		− 0.35	0.7550	1.0000
Size * size	1.19698		0.63	0.5650	1.0000
Size * %A in solvent	1.89644		1.00	0.2976	0.9874
%A in solvent * %A in solvent	− 0.05121		− 0.03	0.9827	1.0000
Size * coal/(A + B)	− 1.16618		− 0.61	0.5773	1.0000
%A in solvent * coal/(A+B)	4.06476		2.13	0.0552	0.3600
Coal/(A + B) * coal/(A + B)	2.00977		1.05	0.2704	0.9762
Size * size * %A in solvent	− 0.18155		− 0.10	0.9335	1.0000

Fig. 2 Screening for five parameters of the definitive screening design (DSD). A: co-solvent (EDA) concentration, A + B: total solvent concentration (NMP + EDA)

Table 7 The responses obtained for the design of the experiments RSM

S. no.	Particle size (µm)	% Co-solvent (A) in solvent (A + B) (vol%)	Coal/solvent (A + B) ratio (wt/vol)	Response (Y) extraction yield (%) (on clean coal product basis)
1	0	− 1	− 1	25.6
2	1	− 1	0	13.3
3	1	1	0	11.2
4	0	− 1	1	22.1
5	1	0	− 1	15.4
6	0	1	1	26.5
7	− 1	0	1	37.3
8	0	0	0	19.4
9	1	0	1	18.5
10	0	0	0	18.1
11	0	1	− 1	24.8
12	− 1	− 1	0	36.2
13	− 1	0	− 1	34.0
14	0	0	0	18.2
15	− 1	1	0	36.0

validation was carried out to obtain the maximum extraction yield according the parameter values given by the prediction profiler (Table 9 and Fig. 3).

The most probable parameter values to obtain the maximum extraction yield were predicted by JMP (11.0) an Minitab(18) were : − 125 µm (particle size), 15% co-solvent (EDA) of total solvent (NMP) concentration and coal to solvent (NMP) ratio as 1:20 (wt/vol). The predicted extraction yield according to JMP(11.0) was 39.5% which was validated through experimentation that gave the

Table 8 Summary of fit

R^2	0.966148
R^2 Adj	0.763036
Root mean square error	4.186088
Mean of response	24.17333

extraction yields of 40.8% on clean coal basis and 39.9% on residual coal basis. This final run was repeated three times and the average extraction yields based on clean coal product basis and loss in weight basis have been presented in Table 9. Figure 4 shows the difference in the predicted values and the experimental values of extraction yields (Table 10).

The parameter values that are obtained through the profiler were found to be for factor X_1 (particle size), X_2 (co-solvent concentration) and X_3 (solvent concentration) are correspondingly of the levels − 1, 1, 1 respectively, i.e. minimizing the particle size and maximizing the co-solvent to solvent ratio and the solvent concentration gives the maximum output i.e. an extraction yield of about 39.5% (Table 9) which has been validated through

experimentation as discussed earlier in the text. The values of the intercepts show the influence of each parameter individually and the interaction profilers show the influence of second order interactions among the parameters. The intercepts show that the influence of the particle size is the highest with a negative maximum intercept and the t-value depicting the increase in output with subsequent decrease in particle size. The impact of the co-solvent and the solvent is not as significant as compared to that of the particle size. The second order interactions show more impact on the extraction yield than the third order. The p-value for particle size factor was found to be closest to 1 further confirming how influential the factor is on the extraction yield and the next influential factor with the second order value is the solvent concentration that shows the relevance of the nature of the solvent for extraction. The measurement (least or highest) of the p-value is indicative of the significance of that factor. The p-value for the particle size ($\gg 0.05$) (Fig. 2) shows the much higher significance of this parameter on the overall extraction yield (significance of 95% confidence interval > 0.05). Using the above

Table 9 Final validation for maximum extraction yield

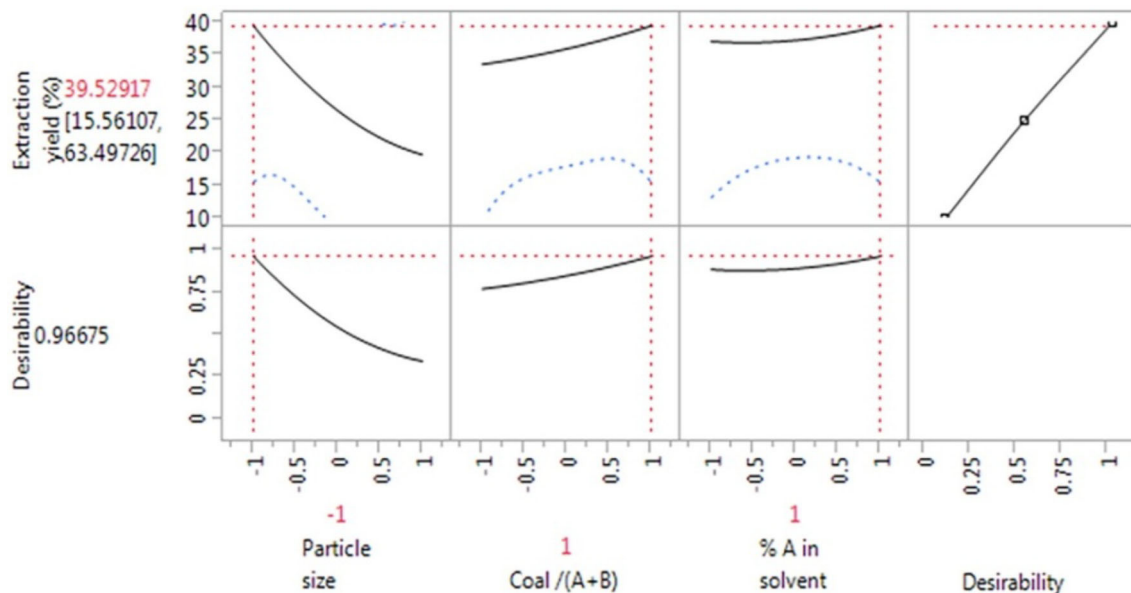| Final experimental validation	Particle size (μm)	% Co-solvent in solvent	Coal/solvent ratio (wt/vol)	Predicted value (%)	Experimental value (clean coal product basis) (%)	Experimental value (loss in weight basis) (%)
16	− 1 (− 125)	1 (15%)	1 (1:20)	39.5	40.87	39.98

Fig. 3 Prediction profiler showing the variation of extraction yields with different parameters and the maximum desirability value

Scatterplot of extraction yield (%) (experimental) vs extraction yield (%) (predicted)
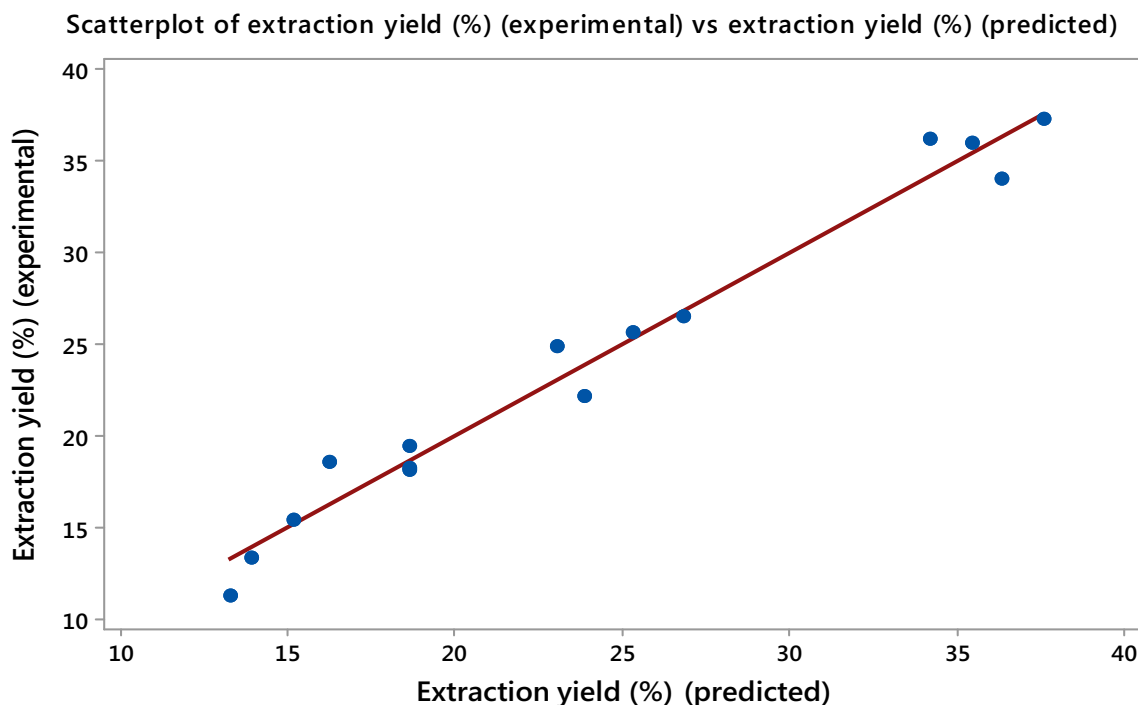

Fig. 4 Plot of difference showing the variation in the extraction yield obtained experimentally and the predicted values through the RSM technique

Table 10 Variation in experimental and the predicted values

Run. no.	Experimental extraction yield (%) (on clean coal product basis)	Predicted extraction yield (%)	Residual extraction yield (%)
1	19.4	18.56	0.84
2	15.4	15.13	0.27
3	36.2	34.17	2.03
4	18.1	18.56	− 0.46
5	26.5	26.78	0.28
6	18.2	18.56	− 0.36
7	37.3	37.56	− 0.26
8	25.6	25.31	0.30
9	34.0	36.31	− 2.31
10	18.5	16.18	2.32
11	24.8	23.03	1.77
12	36.0	35.45	0.55
13	13.3	13.85	− 0.55
14	11.2	13.22	− 2.02
15	22.1	23.86	− 1.76

values, the following equation for the output (extraction yield) based on intercept values (Table 11) has been predicted that helps to study the influence of each individual parameter on the extraction yield:

$$
\begin{aligned}
Y = {} & 20.5666 - 11.925 \times \text{particle size} - 0.45 \\
& \times \text{Coal}/(A + B) \\
& + \text{particle size} \times [\text{particle size} \times 2.5791] \\
& + \text{particle size} \times [\text{Coal}/(A + B) \times - 0.05] \\
& + \text{Coal}/(A + B)[\text{Coal}/(A + B) \times 3.4541] \\
& + \text{particle size} \times [\%A \text{ in solvent} \times - 0.475] \\
& + \text{Coal}/(A + B) \times [\%A \text{ in solvent} \times 1.3] \\
& + \%A \text{ in solvent} \times [\%A \text{ in solvent} \times 1.0291] \\
& + \text{particle size} \times [\text{particle size} \times [\text{Coal}/(A + B) \times 2.05]] \\
& + \text{particle size} \times [\text{Coal}/(A + B) \\
& \times [\text{Coal}/(A + B)2.575]] + \text{particle size} \\
& \times [\text{particle size} \times [\%A \text{ in solvent} \times - 1.475]]
\end{aligned}
$$

3.3 Contour plots

Figures 5, 6 and 7 show the contour plots and the response surface interactions between the different parameters. The response surface plots between the particle size and the % co-solvent in solvent (Fig. 7a) and particle size and coal to solvent ratio (Fig. 7b) are largely elliptical while the plot between the solvent and the co-solvent concentration (Fig. 7c) is parabolic in nature. It shows the major role played by the coal particle size on the extraction yield as it has already been discussed earlier by its intercept values. With the reduction in particle size, the interaction of the coal with the solvents increases. Giri and Sharma (2000) have reported mass transfer effects in the solvent extraction
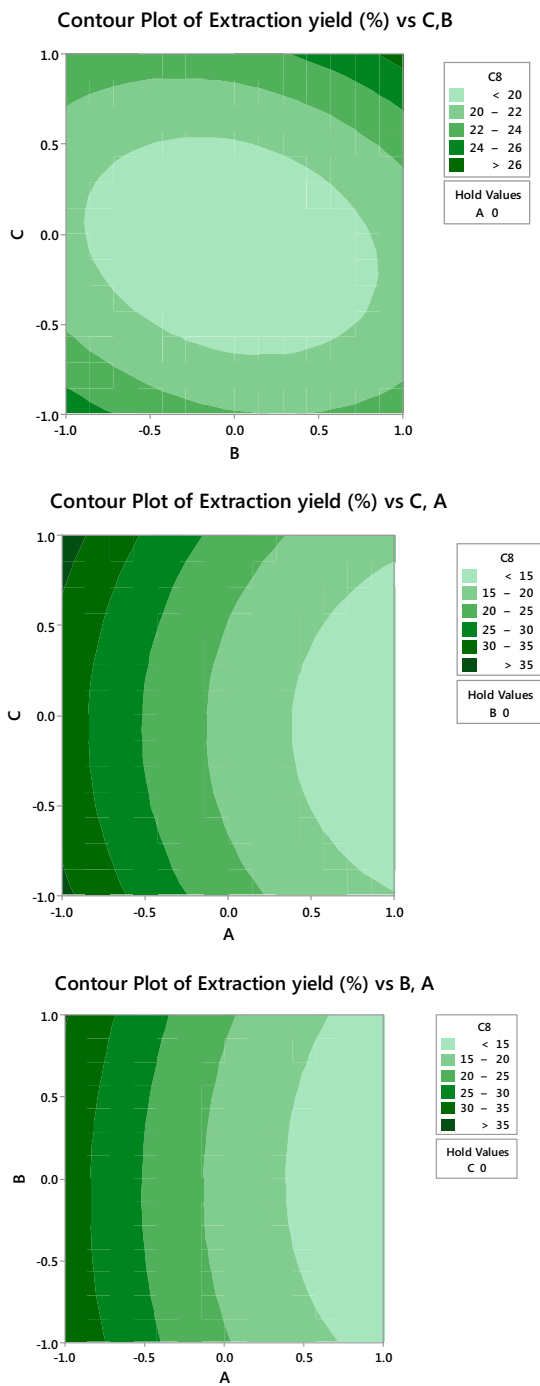
Contour Plot of Extraction yield (%) vs C,B

Contour Plot of Extraction yield (%) vs C, A

Contour Plot of Extraction yield (%) vs B, A

Fig. 5 Contour plots of % extraction yield versus different parameters (A: particle size, B: % co-solvent in solvent, C: total amount of co-solvent + solvent)

of coals. With more surface area available, the solvents NMP and EDA disrupt more coal–coal interactions by breaking H-bonds, π–π interactions, vanderwaal forces and charge transfer interactions. NMP then better interacts with the coal macromolecular structure especially aromatic rings thereby resulting in enhanced extraction (Pande and Sharma 2002; Iino et al. 1988).

Table 11 Screening for Y (% Extraction yield) by RSM Methodology

Term	Scaled estimate	Std. error	t ratio	Prob > t
Intercept	20.56	2.41	8.51	0.0135
Particle size	$-$ 11.92	2.09	$-$ 5.70	0.0295
Coal/(A + B)	$-$ 0.45	2.09	$-$ 0.21	0.8497
% A in solvent	0.9	2.09	0.43	0.7091
Particle size * particle size	2.57	2.17	1.18	0.3581
Particle size * coal/(A + B)	$-$ 0.05	2.09	$-$ 0.02	0.9831
Coal/(A + B) * coal/(A + B)	3.15	2.178	1.45	0.2846
Particle size * % A in solvent	$-$ 0.47	2.09	$-$ 0.23	0.8416
Coal/(A + B) * % A in solvent	1.3	2.09	0.62	0.5979
% A in solvent * % A in solvent	1.02	2.17	0.47	0.6832
Particle size * particle size * coal/(A + B)	2.05	2.96	0.69	0.5602
Particle size * coal/(A + B) * coal/(A + B)	2.57	2.96	0.87	0.4761
Particle size * particle size * % A in solvent	$-$ 1.47	2.96	$-$ 0.50	0.6677

3.4 Regression analysis

Minitab^{TM} (version 18) was used for the regression analysis. The quality of the multiple regression model fitting was measured by calculating the coefficient of regression R^2. F test was used for testing its statistical significance. The analysis of variance test was used to calculate the significance of these linear parameters on the extraction yield. The results of which have been given in Table 12. The results again predict the much higher effect of the particle size on the extraction yield with the least p value and highest F value (Segurola et al. 1999). Thus the regression analysis was found to be in conformity with the design of experiments methodology.

3.5 Solvent recovery

Solvent recovery was also noted during the course of these extraction studies and the amounts of NMP and EDA recovered are shown in Table 13. The high recovery (greater than 90%) of NMP and EDA solvents in this process seems to be a step towards making the process economically attractive in future for the possibility of its use (Chandaliya et al. 2015).
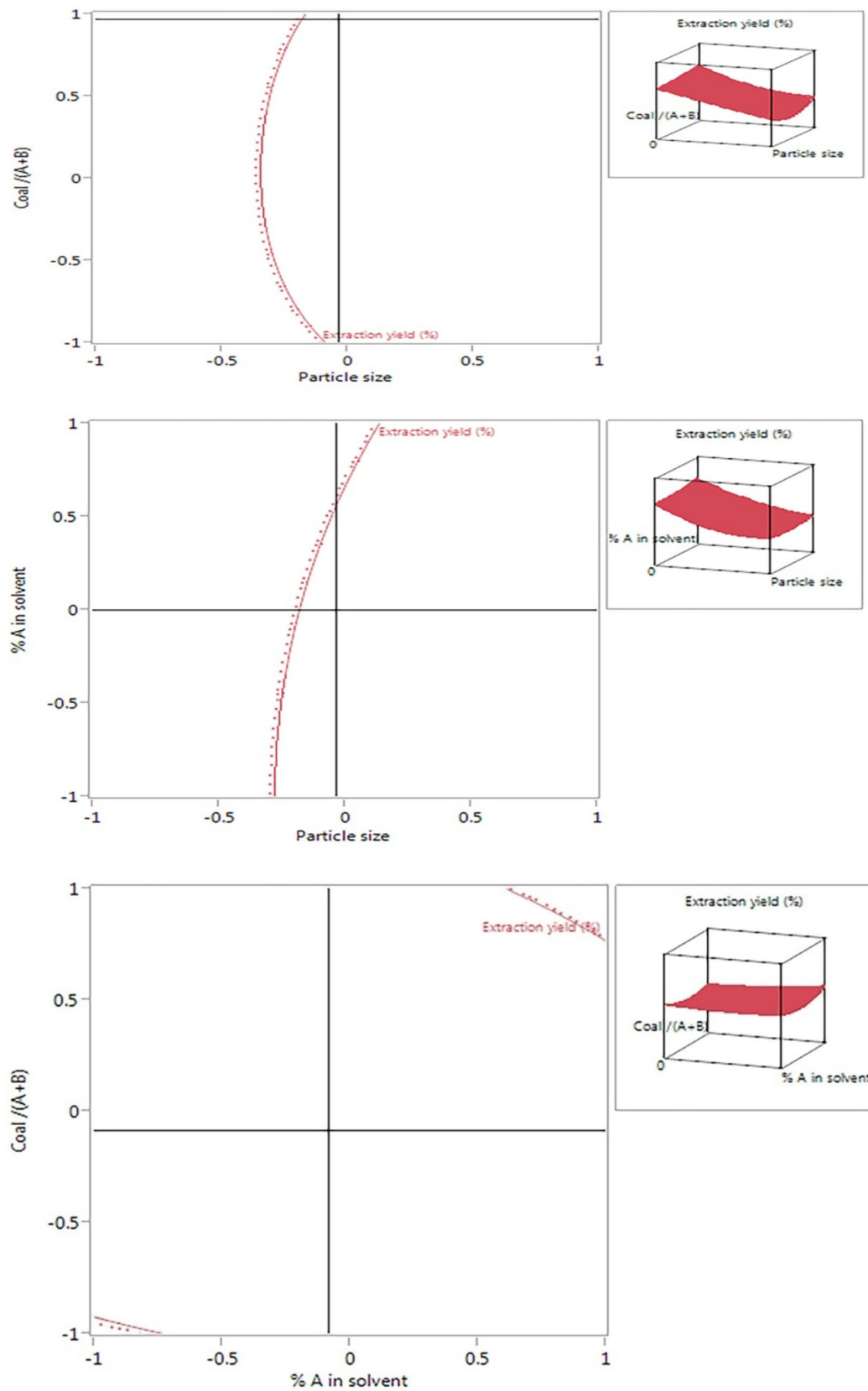
Fig. 6 Contour profilers for the parameters keeping one parameter constant and varying the other two [A: amount of co-solvent (EDA), A + B: total amount of co-solvent + solvent (EDA + NMP)]
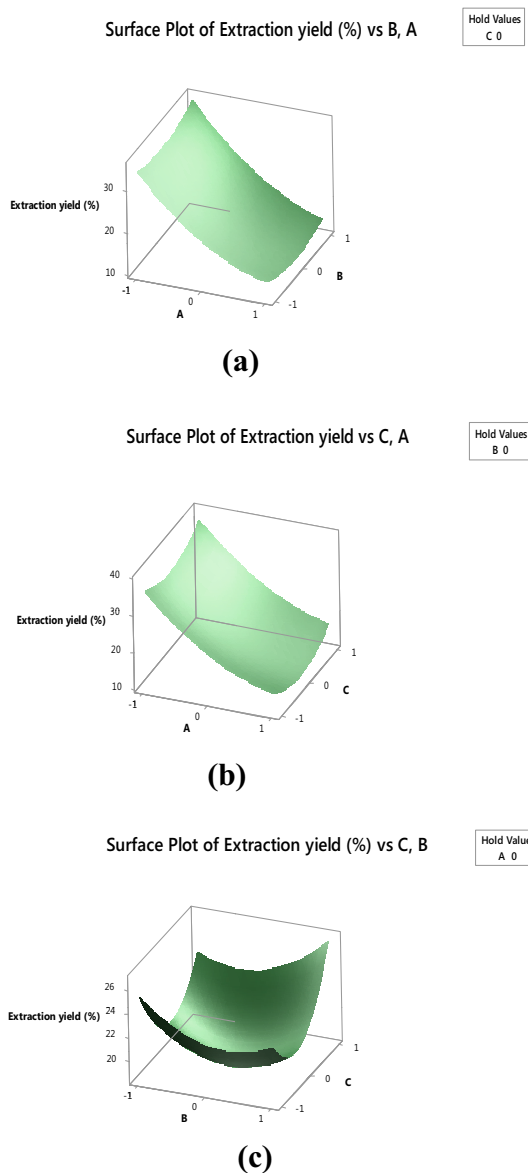
Surface Plot of Extraction yield (%) vs B, A

Hold Values
C 0

(a)

Surface Plot of Extraction yield vs C, A

Hold Values
B 0

(b)

Surface Plot of Extraction yield (%) vs C, B

Hold Values
A 0

(c)

Fig. 7 Response surface plot showing the predicted values of the extraction yield with effect on particle size (A) and % co-solvent in solvent (B) (**a**), particle size with coal/total amount of co-solvent + solvent (C) (**b**) and % co-solvent in solvent (B) and coal/total amount of co-solvent + solvent (C) (**c**) [A: amount of co-solvent (EDA), A + B: total amount of co-solvent + solvent (EDA + NMP)]

4 Conclusions

Solvent extraction of a high ash, low grade non-coking Indian coal, Kedla coal was performed using pre-treatment with acetic acid followed by extraction with NMP and EDA. Optimization of the extraction parameters was carried out. Using Definitive Screening Design for optimization of five parameters and RSM–Box Behnken experimental design for 3 parameters, maximum extraction yield under the given set of conditions was obtained. About

Table 12 Analysis of variance model regression on extraction yield

Source	DF	Adj SS	Adj MS	F value	p value
Regression	3	908.11	302.702	26.18	0.000
Particle size	1	905.25	905.251	78.30	0.000
%A in solvent	1	0.21	0.211	0.02	0.895
Coal/A + B	1	2.64	2.645	0.23	0.642
Error	11	127.18	11.562		
Lack-of-fit	9	92.14	10.237	0.58	0.766
Pure error	2	35.05	17.523		
Total	14	1035.2			

R^2: 87.72%, R^2 (adj.): 84.36%, R^2 (pred.): 80.80%

DF, degree of freedom; SS, sum of squares; MS, mean of squares; F, F value; p, significance

Level of P-value (a significance level < 0.05)

Table 13 Amount of solvents recovered during the extraction process

Solvents used for extraction	NMP	EDA
Amount of solvents used (%)	100.0	100.0
Solvents recovered (%)	92.0	90.0
Unaccounted loss (%)	8.0	10.0

39.5% of the extraction yield could be achieved with maximum desirability output for these parameters obtained using the design of experiments (DSD and RSM) technique i.e. the particle size less than 125 micron, co-solvent to solvent concentration (vol%) of 15% of the total solvent concentration and the coal to solvent ratio as 1:20 (wt/vol). This technique also shows the linear and square interaction effects of the different parameters. The RSM model and the intercept values show the maximum impact of the coal particle size on the extraction yield. The regression analysis was found to be in good agreement with the RSM responses. This extraction process makes use of mild atmospheric pressure conditions unlike the high pressure and temperature conditions that make use of hydrogenating solvents where the clean coal product recovery is extremely difficult. Design of experiments reduces the number of experimental runs to be performed for optimization. The clean coal extraction yield is relatively high and this optimization consumes fewer amounts of the solvents. This technique results in leading to the conditions on obtaining enhanced amount of super clean coal without resorting to large number of experiments of process intensification studies on the organo-refining of power grade coal using the designer e, N solvent system. Organo-refining is an

emerging clean coal technology and there is a need to make it economical. Present study is a step in this direction.

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