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Comparison of rCCD and BBD design for reactive separation of gallic acid using trioctylamine in lauryl alcohol

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Rotatable Central Composite Designs (rCCD) and Box–Behnken Design (BBD) have been used as statistical multivariate methods in the optimization of reactive separation of gallic acid from the aqueous solutions using trioctylamine as extractant dissolved in lauryl alcohol. Effects of variable such as initial concentration of gallic acid (0.02- 0.04 kmol.m^{-3}), extractant (20–40%, v/v in diluent), temperature (298-318 K) on the separation efficiency of gallic acid have been investigated. rCCD model predicted the maximum separation efficiency of 84.54% at the conditions of initial acid concentration (0.031 kmol.m^{-3}), extractant volume percentage (17.20 % v/v in diluent) and temperature (298 K) as the optimal solution. BBD model suggested that the optimum conditions are initial acid concentration (0.031 kmol.m^{-3}), extractant volume percentage (17.82 %v/v in diluent) and temperature (298.68 K) provided separation efficiency of 83.71%. The exactness of the two models is judged based on the actual experiments at some random points. Results indicate that the rCCD and BBD are both are reasonably accurate with rCCD slightly more accurate as shown by lower residual square error obtained using the values predicted by both the models.

Keywords: BBD, Gallic acid separation, Lauryl alcohol, rCCD, Reactive separation, Trioctyl amine

Introduction

Gallic acid is important phenolic acid possessing vast medicinal properties[1]. It is produced chemically by the hydrolysis of tannins industrially[2]. Alternative methods of production include the bio-conversion of tannins by naturally produced enzyme tannase which is produced by variety of microbes[3-6]. The recovery of gallic acid from such bioconversion broth/fermentation media is a complex process and there are various methods available[7]. Currently, the used methods have some limitations. Method like precipitation[8] involves high production of sludge and toxic compounds. Sorption[9] is another method but drawback includes limited capacity of solid surface, membrane separation being in developmental stage[10-11]. Out of the several methods examined in the literature, reactive separation is an emerging technology for the effective recovery of carboxylic acids from fermentation broths and model solutions[12-14]. Some studies can be found in literature for gallic acid reactive separation[15-18]. Reactive extraction of gallic acid from aqueous solutions with various extractants such as tri-n-butyl Phosphate, tri-n-octylamine and aliquat 336 in two diluents have been carried out by Rewatkar *et al.*[16]. Pandey *et al.*[17] examined the efficiency when two different extractants such as tributyl phosphate and trioctyl amine are used in four different diluents such as n-decane, MIBK, 1-octanol and kerosene and concluded that TOA was good with active diluents such as octanol and MIBK whereas tri butyl phosphate was good with inactive solvents n-decane and kerosene. Joshi *et al.*[18] have used tributyl phosphate with four different solvents such as ethyl acetate, n-hexane, 1-octanol and toluene for the reactive separation of gallic acid and concluded that tributyl phosphate was highly efficient when used with inactive solvents such as toluene and n-hexane. Though there are equilibrium studies available but more knowledge regarding the optimum values of parameters such as extractant volume %, temperature and initial acid concentration can be obtained by the use of techniques such as Response Surface Methodology (RSM).

RSM technique uses statistics to analyse and optimize the input parameters. It is based on developing a model polynomial equation that describes the behaviour of the system at different input variables. The equation can then be solved for optimizing (maximizing or minimizing) the given objective function. Rotatable Central Composite Design (rCCD) and Box-Behnken design (BBD) are frequently employed designs for RSM. Modelling and optimization of the reactive separation of gallic acid by RSM and

ANN has also been carried out by some authors[19-21]. But there is no study comparing the two different type of RSM models such as rCCD and BBD for the reactive separation of gallic acid. Therefore, present work reports the comparative analysis of rCCD and BBD for the reactive separation of gallic acid from the aqueous solutions using trioctylamine as extractant dissolved in lauryl alcohol.

Experimental Section

Materials

Gallic acid [$(OH)_3C_6H_2CO_2H.H_2O$] was procured from Molychem, India, having purity 99.5%. The extractant trioctyl amine ($C_{24}H_{51}N$) was procured from SRL Pvt. Ltd having purity 95%. Lauryl alcohol was obtained from the manufacturer Pallav, India. The chemicals were used directly without using any purification method as they were relatively pure. The aqueous solutions of gallic acid were made in ultrapure water (obtained from Millipore water purifier).

Method

As the concentration of gallic acid is very less (<0.058 kmol.m^{-3}) in wastewater and in the fermentation media[18], all the experiments were carried out within the range 0.02-0.04 kmol.m^{-3}. The concentration of extractant (TOA) was varied in the range of 10-30% v/v in the diluent lauryl alcohol. The equilibrium experiments involve shaking of equal volumes of aqueous and organic phases for 5 h at different temperature (298 – 318 K) in water bath shaker followed by settling of the mixture for at least 2 h at the shaking temperature. Aqueous phase acid concentration was determined by analysis by UV-visible spectrophotometer at the wavelength of 264 nm. The acid content in the organic phase was determined by mass balance.

The distribution coefficient (K_D) was calculated by dividing the concentration of acid in the organic phase by concentration of acid in the aqueous phase as given by Eq. (1)

$$K_D = [HA]_{org}/[HA]_{aq} \quad \ldots (1)$$

The separation efficiency (η %) can be obtained from the Eq. (2)

$$\eta = \frac{K_D}{1+K_D} \quad \ldots (2)$$

Experimental design

For the rCCD upper and lower points of confinement of the procedure factors were resolved and the quantitative qualities were changed to their regarded coded values as far as ±1, 0 and ± α. Table 1 shows the limits, units and notations of input variables. For rCCD having three independent input variables (n =3), the experiments (N) to be conducted are calculated as

$$N= (2^n+ 2n+ n_c) = 2^3+2*3+ 6 = 20, \quad \ldots (3)$$

where n represents the total number of input factors; n_c represents the number of times the central pointy is repeated. The value of alpha (α) was calculated by Eq. 4.

$$\alpha = 2^{(k-n)/4} \quad \ldots (4)$$

Where k is number of repeatable runs and n is number of factors.

A comparison between the rCCD and BBD was made after the experiment were analysed for both the design matrix. Results were statistically analysed by using Design Expert version 11.0.3.0 by Stat-Ease Inc.

Experimental data were observed and separation efficiency was regressed and fitted to a second order polynomial model equation as follows:

$$\eta = \beta_o + \beta_1(A) + \beta_2(B) + \beta_3(C) + \beta_4(A*B) + \beta_5(A*C) + \beta_6(B*C) + \beta_7(A^2) + \beta_8(B^2) + \beta_9(C^2) \quad \ldots (5)$$

Table 1 — Independent variables and their values used for central composite rotatable design and Box Behnken design

Factor	Code	Levels				
		-α	-1	0	1	+α
rCCD						
Initial gallic acid conc. (mol.m^{-3})	A	0.0131	0.02	0.03	0.04	0.046
Extractant conc. (% v/v in diluent)	B	3.18	10	20	30	36.81
Temperature (K)	C	291.182	298	308	318	324.818
BBD						
Initial gallic acid conc. (mol.m^{-3})	A	-	0.02	0.03	0.04	-
Extractant conc. (% v/v in diluent)	B	-	10	20	30	-
Temperature (K)	C	-	298	308	318	-

Where, β_o is regression coefficient for constant term, β_1, $\beta 2$ and $\beta 3$ are regression coefficient for linear terms, β_4 , β_5 and β_6 are regression coefficient for interactive terms, β_7 , β_8 and β_9 are regression coefficient for quadratic terms, respectively. A, B and C are independent variables.

Statistical analysis

Analysis of variance (ANOVA) is carried out to find out the effect of different input parameters independent, interactive and quadratic effects on the separation efficiency. Regression was carried out to fit the values of separation efficiency to polynomial equation as described by Eq. (5).

Verification of models

To verify the accuracy of the models generated four random experiment were conducted. The separation efficiency obtained in each random experiment was compared with the predicted value obtained by the regression equation for both the rCCD and BBD models. Percentage of residual standard error (RSE) was calculated for each response.

Results and Discussion

Fitting the models

Composition factors on the response of separation efficiency which was acquired experimentally based on rCCD and BBD matrix are tabulated in Table 2. The predicted values are in agreement with the experimental values in almost all cases. Polynomial model equation in terms of the actual variables for the rCCD and BBD are as follows:

rCCD: $\eta(\%)= 2526.997 + (-3729.86663*A) + (1.16627*B) + (-15.075*C) + (0.225*A*B) + (24.675*A*C) + (-0.001175*B*C) + (-56734.831*A^2) + (-0.0239*B^2) + (0.022355*C^2)$ … (6)

BBD: $\eta(\%) = 2499.6181 + (-3631.475*A) + (1.0494*B) + (-14.899*C) + (1.25*A*B) + (24.375*A*C) + (-0.0009*B*C) + (-57077.499*A^2) + (-0.0234*B^2) + (0.0220*C^2)$ … (7)]

ANOVA results of the quadratic models for the separation efficiency are tabulated in Table 3 and Table 4. For any terms in the models, high F-value and small P-value would indicate more significant effect on the respective response variables. Thus, the variables with the largest effect on the separation efficiency was the temperature ($P < 0.0001$, $F = 4219.91$), followed by initial acid concentration ($P < 0.0001$, $F = 2697.76$) and extractant volume % ($P < 0.0001$, $F = 259.43$). The P-value was smaller than 0.05 which indicated most terms of the models were still significant. Pure errors such as experimental errors were minimal (rCCD = 0.108; BBD = 8E-05) for both designs.

Table 2 — Experimental and Predicted values of separation efficiency(η) at different input variable initial acid concentration (A), extractant volume % (B) and temperature (C) by BBD and rCCD model

	BBD						rCCD				
Run	A	B	C	ηExp.	ηPred.	Run	A	B	C	ηExp.	ηPred.
1	0.03	30	298	80.50	80.44	1	0.03	20	291.18	91.20	92.24
2	0.03	10	318	71.45	71.51	2	0.04	10	298	79.50	79.63
3	0.04	20	298	80.71	80.75	3	0.04	10	318	72.84	73.03
4	0.02	20	318	59.45	59.41	4	0.03	3.18	308	72.02	71.71
5	0.03	20	308	76.01	76.02	5	0.02	10	298	75.59	75.20
6	0.03	10	298	83.08	83.12	6	0.03	36.81	308	66.50	66.80
7	0.04	20	318	73.80	73.82	7	0.03	20	308	76.02	76.02
8	0.03	20	308	76.02	76.02	8	0.013	20	308	52.00	52.06
9	0.04	10	308	74.12	74.04	9	0.046	20	308	68.00	67.88
10	0.02	10	308	64.79	64.76	10	0.02	10	318	58.12	58.73
11	0.03	30	318	68.49	68.45	11	0.02	30	298	72.65	72.47
12	0.02	20	298	76.11	76.09	12	0.02	30	318	55.65	55.53
13	0.03	20	308	76.02	76.02	13	0.04	30	318	69.72	69.92
14	0.03	20	308	76.02	76.02	14	0.03	20	308	76.25	76.02
15	0.04	30	308	71.39	71.42	15	0.03	20	308	76.04	76.02
16	0.02	30	308	61.56	61.64	16	0.03	20	308	75.86	76.02
17	0.03	20	308	76.02	76.02	17	0.03	20	324.81	73.00	72.45
						18	0.03	20	308	75.86	76.02
						19	0.03	20	308	76.08	76.02
						20	0.04	30	298	77.69	76.99

Table 3 — ANOVA results for the experimental results of rCCD

	Sum of Square	df	Mean Square	F value	p value	Remarks
Model	1494.425	9	166.0472	1482.073	<0.0001	significant
A-Initial acid conc.	302.2495	1	302.2495	2697.76		
B-Extractant conc.	29.06568	1	29.06568	259.4288	<0.0001	significant
C-Temperature	472.7864	1	472.7864	4219.906	<0.0001	significant
AB	0.00405	1	0.00405	0.036149	0.8530	insignificant
AC	48.70845	1	48.70845	434.7525	<0.0001	significant
BC	0.11045	1	0.11045	0.985833	0.3442	insignificant
AÂ²	463.8766	1	463.8766	4140.38	<0.0001	significant
BÂ²	82.49157	1	82.49157	736.2874	<0.0001	significant
CÂ²	72.02025	1	72.02025	642.8245	<0.0001	significant
Residual	1.120372	10	0.112037			
Lack of Fit	1.012289	5	0.202458	9.365815	0.0141	
Pure Error	0.108083	5	0.021617			
Cor Total	1495.546	19				

Table 4 — ANOVA results for the experimental results of BBD

	Sum of Square	df	Mean Square	F value	p value	Remarks
Model	680.3829	9	75.5981	18728.96	<0.0001	significant
A-Initial acid conc.	181.5465	1	181.5465	44977.02	<0.0001	significant
B-Extractant Conc.	16.53125	1	16.53125	4095.514	<0.0001	significant
C-Temperature	278.598	1	278.598	69020.92	<0.0001	significant
AB	0.0625	1	0.0625	15.48399	0.005	insignificant
AC	23.76563	1	23.76563	5887.785	<0.0001	significant
BC	0.0361	1	0.0361	8.94355	0.0202	insignificant
A^2	137.1723	1	137.1723	33983.57	<0.0001	significant
B^2	23.15873	1	23.15873	5737.43	<0.0001	significant
C^2	20.51348	1	20.51348	5082.088	<0.0001	significant
Residual	0.028255	7	0.004036			
Lack of Fit	0.028175	3	0.009392	469.5833	<0.0001	
Pure Error	8E-05	4	2E-05			
Cor Total	680.4112	16				

Response Surface Analysis

Effect of initial concentration of gallic acid on separation efficiency

The effect of initial concentration of gallic acid on the separation efficiency at a fixed concentration of trioctylamine at 20% (v/v) in lauryl alcohol and temperature of 308 K is presented in Fig 1. It can be observed that as the initial acid concentration increases from 0.02 kmol.m^{-3} to 0.035 kmol.m^{-3} the separation efficiency increases. The reason for such behaviour may be due to the fact that with the increase in initial acid concentration there is high concentration gradient that causes high mass transfer of acid to the organic phase. On further increasing the initial acid concentration beyond 0.35 kmol.m^{-3}, the separation efficiency becomes constant.

Effect of extractant volume % (TOA) on separation efficiency

The effect of extractant volume % of trioctyl amine on the separation efficiency at a fixed initial acid concentration of gallic acid at 0.03 kmol.m^{-3} and

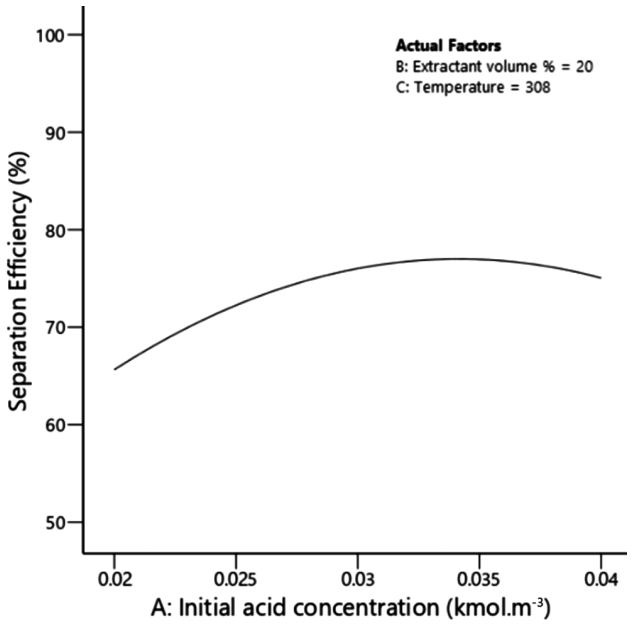

Fig. 1 — Variation of separation efficiency with initial acid concentration

temperature of 308 K is presented in Fig 2. On increasing the extractant TOA concentration from 10 %(v/v) in lauryl alcohol to 20 % (v/v) in lauryl alcohol, the separation efficiency remains constant as the extractant is present in very high amount (10 % v/v = 0.2287 kmol.m^{-3}) initially itself and further increase of extractant has no effect on the separation efficiency. A very high concentration of TOA (30 % v/v and above) may cause slight decrease in the separation efficiency as the viscosity increases on addition of TOA which may hinder the mass transfer process.

Effect of temperature change on separation efficiency

The effect of temperature on the separation efficiency at a fixed initial acid concentration of gallic acid at 0.03 mol.m^{-3} and extractant volume % of trioctyl amine at 20 % (v/v) is presented in Fig 3. On increasing the temperature of operation from the 298 K to 318 K, the separation efficiency decreases which may due to the fact that reactive extraction is usually an exothermic process and is therefore favourable at low temperatures.

Effect of initial acid concentration and TOA concentration on separation efficiency

The effect of initial gallic acid and TOA concentration on separation efficiency at a fixed temperature of 308 K is presented in Fig 4(a) and (b). It can be observed that optimum separation efficiency is observed at moderate concentration of extractant

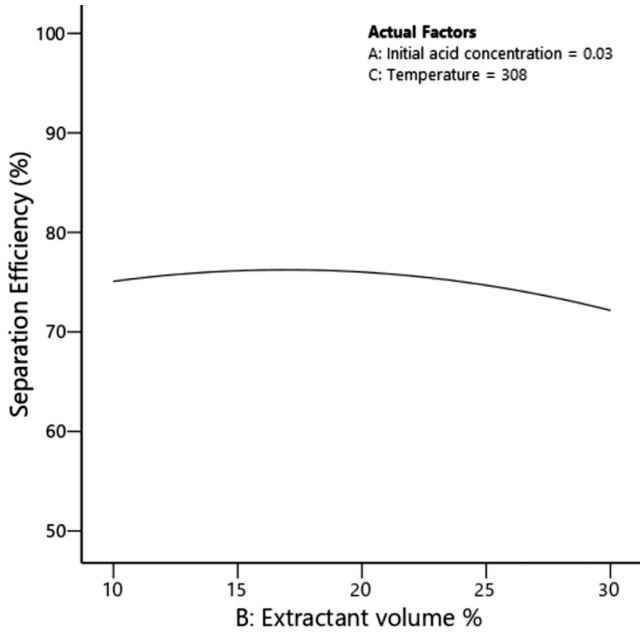

Fig. 2 — Variation of separation efficiency with extractant volume %

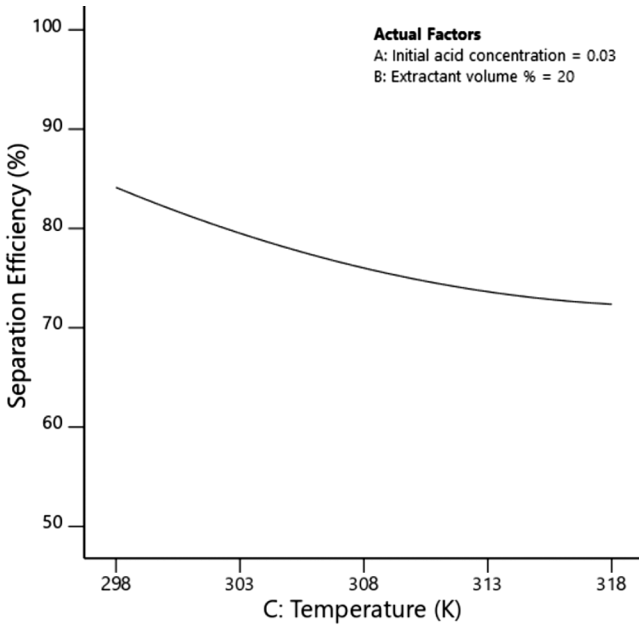

Fig. 3 — Variation of separation efficiency with temperature

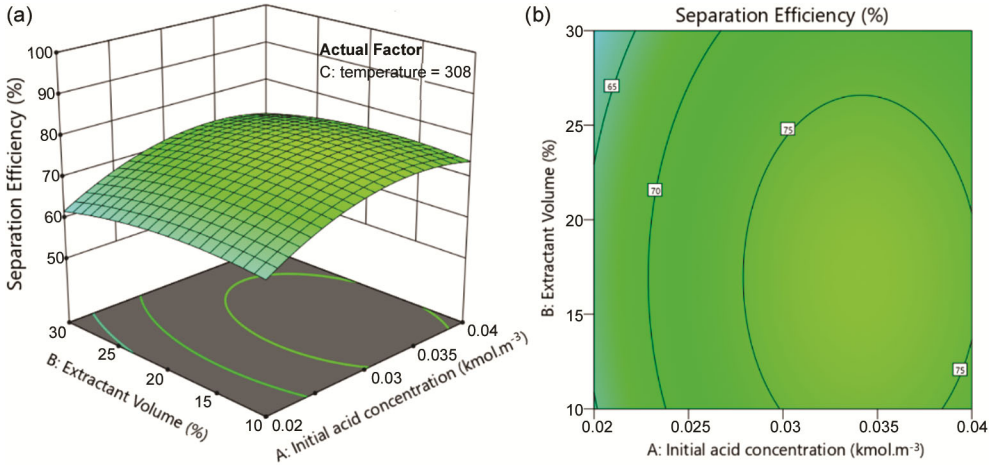

Fig 4 — (a) 3d plot and (b) Contour plot for variation of separation efficiency with initial acid concentration and extractant volume %

TOA and initial acid concentration of 0.03-0.04 mol.m^{-3}.

Effect of temperature and TOA concentration on separation efficiency

The effect of TOA concentration and temperature on separation efficiency at a fixed initial acid concentration of 0.03 mol.m^{-3} is presented in Fig 5(a) and (b). It can be observed that maximum separation efficiency is observed near 298 K temperature and 10-25 % (v/v) concentration of TOA

Effect of temperature and gallic acid concentration on separation efficiency

The effect of temperature and initial gallic acid concentration on separation efficiency at a fixed initial acid concentration of 0.03 kmol.m^{-3} is presented in Figs 6(a) and (b). It can be observed that maximum separation efficiency is observed near 298 K temperature and initial acid concentration of 0.025 to 0.04 mol.m^{-3}.

Optimization of process variables by rCCD and BBD

The optimum conditions are where maximum separation efficiency is observed. The optimization of the reactive separation process was done by both rCCD and BBD and the two model predicted similar results. The rCCD predicted the optimum(maximum) separation efficiency of 84.54% at the conditions of initial acid concentration (0.031 kmol.m^{-3}), extractant volume % (17.20 % v/v in diluent) and temperature (298 K), whereas the BBD predicted the maximum efficiency of 83.71% at initial acid concentration (0.031 kmol.m^{-3}) extractant volume % (17.82 % v/v in diluent) and temperature (298.68 K). The separation efficiency at the optimum conditions were also checked at it was observed that the actual value is very near to the value predicted by both the models.

Comparison of rCCD and BBD

Presence of rotated lower dimensional design in Box Behnken design estimates the linear/quadratic/

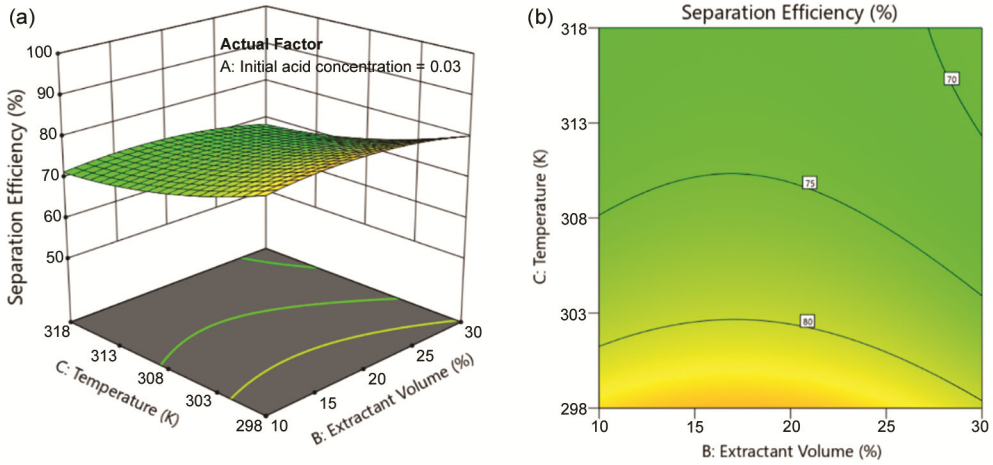

Fig 5 — (a) 3d plot and (b) Contour plot for variation of separation efficiency with temperature and extractant volume %

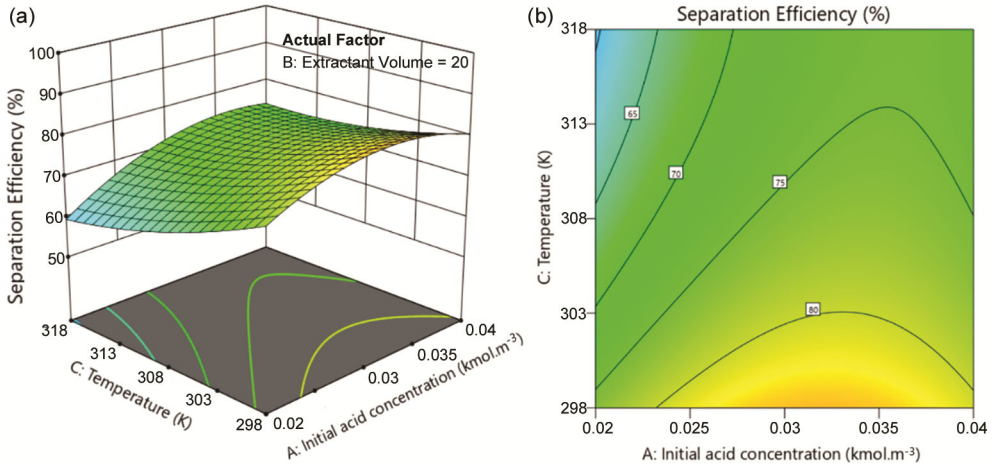

Fig 6 — (a) 3d plot and (b) Contour plot for variation of separation efficiency with temperature and initial acid concentration

Table 5 — Predicted and actual value for separation efficiency at some randomly observed points

Run	Independent variable			Response variable	rCCD		BBD	
	Initial acid concentration ($mol.m^{-3}$)	Extractant volume (%)	Temperature (K)	Efficiency experimental	Efficiency predicted	RSE	Efficiency predicted	RSE
1	0.025	15	303	76.61	76.72	0.143	76.41	0.261
2	0.035	15	303	75.25	75.31	0.079	74.96	0.385
3	0.025	25	303	61.75	61.91	0.259	61.51	0.388
4	0.035	25	303	60.14	60.48	0.565	59.94	0.892

two way interactions. However the shortcomings in Box Behnken design is that it does not allow the reduction in design and non-flexible nature. On the contrary, cube part of rCCD contributes to main and interactive influences whereas main and quadratic are measured by factor alpha in rCCD. In additions the presence of off bound axial point defined by factorial parts, results in rotatability, which allows response prediction with equal variance irrespective of direction of centre of the design space.

Comparison between rCCD and BBD methods was assessed in random conditions for the separation efficiency. Table 5 showed the effects of three independent variables on the experimental value along with the predicted values for the separation efficiency. The residual standard error is calculated as

$$Residual\ standard\ error(\%) = \frac{Exp.Value - Pred.Value}{Exp.Value} * 100 \quad \ldots (8)$$

Conclusion

Experimental design is an excellent tool to analyse and optimize the reactive separation of gallic acid from the aqueous solutions using trioctylamine as extractant dissolved in lauryl alcohol. All the factors chosen factors such as initial acid concentration, extractant volume percentage and temperature had a significant effect on the response variable (separation efficiency) .The results of the present study showed that the rotatable central composite design predicts responses closer to the actual values as compared to the Box–Behnken design based on the residual standard error analysis.

Conflict of interest

The authors declare no conflict of interest.

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