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Optimize conditions for extracting crude oil from Alliums cepa. L. var. agrogatum Don using response surface methodology

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Abstract

The crude oil extracts from Alliums cepa. L. var. agrogatum Don was carried out organic solvent extraction. Use response surface methodology (RSM) to optimize the experimental factors: extraction temperature, extraction time and liquid-solid ratio. The crude oil extracts content was accomplished by Gas chromatography–Mass Spectrometry (GC-MS). The data suggests that the extraction rate of crude oil was effected by the extraction time significantly. The optimum conditions of Alliums cepa. L. var. agrogatum Don crude oil extraction were: extraction temperature 72℃, extraction time 4h and liquid-solid ratio 14:1. As the results of GC-MS showed the content of linoleic acid was 7.661%.

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Keywords: Alliums cepa. L. var. agrogatum Don, Gas Chromatography–Mass Spectrometry, Response surface methodology, Crude oil

1. Introduction

Alliums cepa. L. var. agrogatum（ACAD）, which was mainly produced in Northeast China, was high-yielding crop. At the same time, ACAD was a kind of well-known health foods which was called soft gold of glycolipid regulation. The geographic latitude, accumulated temperature, precipitation, soil and light in the Changbai Mountain makes special growth conditions for ACAD to have high special nutrients. It is reported

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that there were at least six ingredients which were good for anti-cancer, anti-aging and lipid-lowering. ACAD was also good for brain tumors, breast and prostate.

It is reported that there were 18 kinds of trace elements and 17 kinds of amino acids which had been determined [1]. In 2009, Zhen Yang Liu optimized the conditions of supercritical carbon dioxide extraction of ACAD by single factor and orthogonal experiments.

Volatile oil which was also called essential oil was a kind of volatility oily liquid distilled with water vapor. The fragrance of ACAD was mainly derived from essential oil. At present, the methods of the essential oil extraction were mainly steam distillation, organic solvent extraction and supercritical CO_2 extraction [3-4]. In the three methods, steam distillation need higher temperature which maybe destructed the active ingredients and supercritical extraction CO_2 had higher cost. So, this work choses organic solvent extraction as the extraction method.

It's good for response surface methodology (RSM) to affect parameters which have an impact on many factors and their mutual influence, which was firstly depicted by Box and Wilson [5]. A lot of studies pointed out that it is available for developing, improving and optimizing processes [6-7].

This work described a method of the extraction of ACAD essential oils and optimized the conditions by the RSM.

2. Materials and methods

2.1. Materials

ACAD was purchased from local supermarket. All chemicals/solvents used were of analytical grade. Petroleum ether was purchased from Beijing Chemical Works. Gas Chromatography Mass was Agilent 5975.

2.2. Single factor experiment of the extraction of crude oil from ACAD

Choose the extraction temperature(65℃,68℃,71℃,74℃,77℃), extraction time (2.5h,3h,3.5h,4h,4.5h) and liquid-solid ratio(8:1,10:1,12:1,14:1,16:1) as the single factor to investigate the extraction conditions of crude oil.

Weight 3 copies of the ACAD accurately into 5 flasks, respectively. And every flask had 5g of ACAD. Measured petroleum ether 40mL,50mL,60mL,70mL and 80mL into the above three flasks, respectively. Then the five flasks were heated in the digital display constant temperature water bath at 65℃for 3h. Then filter the extraction and retain the filtrate. Used the rotary evaporators to volatile the solvent and the rest was crude oil of ACAD.

Weight three copies of the ACAD accurately into 5 flasks, respectively. And every flask had 5g of ACAD. Measured petroleum ether 70mL into the above five flasks. Then the three flasks were heated in the digital display constant temperature water bath at 65℃,68℃,71℃,74℃,77℃for 3h, respectively. Then filter the extraction and retain the filtrate. Used the rotary evaporators to volatile the solvent and the rest was crude oil of ACAD.

Weight 3 copies of the ACAD accurately into 5 flasks, respectively. And every flask had 5g of ACAD. Measured petroleum ether A.R. Ⅱ70mL into the above five flasks. Then the five flasks were heated in the digital display constant temperature water bath at 65℃ for 2.5h, 3h, 3.5h, 4h and 4.5h, respectively. Then filter the extraction and retain the filtrate. Used the rotary evaporators to volatile the solvent and the rest was crude oil of ACAD.

2.3. Using response surface methodology to optimize extracting conditions

Based as the single factor experiment, optimized the extracting conditions via using response surface analysis which had choose the yield of crude oil as the dependent variable.

2.4. Determination of ACAD oils by Gas Chromatograph-Mass Spectrometry (GC-MS)

Analyses of ACAD crude oil was implemented by a Agilent 5975 GC-MS system with flame ionization detector (FID), and nitrogen was the carrier gas at a linear flow rate of 20mL.A fused silica capillary column with a stationary phase equivalent to Carbowax 20M, with dimensions 50m × 0.32mm and 1.0μm film thickness was used. The temperature of the column was procedured firstly at 40℃ for 2min and then increased at a velocity of 5℃ to 120℃ for 5min and then increased at a velocity of 10℃ to a final temperature 250℃ for 5min. Injector and detector temperature were both retained at 270℃. It was 1μL for each injection.

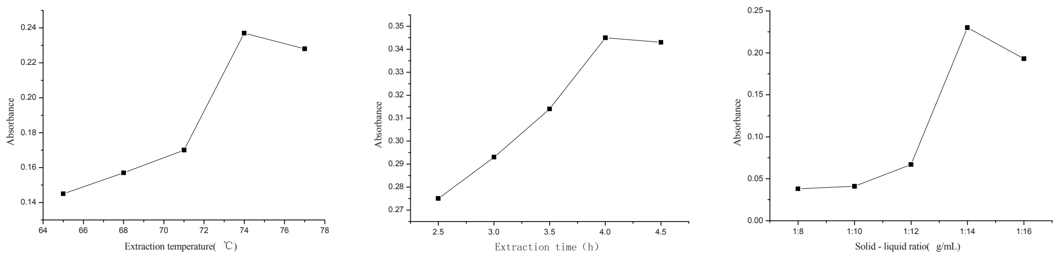
The volatile compounds in extracts were determined by Gas Chromatography–Mass Spectrometry (GC-MS) with computerized integrated data processing and retention indices.

3. Statistical analysis

All data are presented as the mean ± SE. The data was performed if differences were identified between the groups at $p < 0.05$.

4. Results and discussions

4.1. The results of single factor experiment



(a) (b) (c)

Fig.1. The effect of single factor experiment, extraction temperature, extraction time and liquid-solid ratio, to ACAD crude oil extraction. Fig. 1(a) was the effect of extraction temperature to ACAD crude oil extraction. Fig.1(b) was the effect of extraction time to ACAD crude oil extraction. Fig. 1(c) was the effect of liquid-solid ratio to ACAD crude oil extraction.

4.2. The results of response surface methodology

This study used Box–Behnken design combined with RSM to optimize the operational parameters. The optimized experiment involved the three parameters extraction temperature, extraction time and liquid-solid ratio according to the Box–Behnken design.

Table.1. Box-Behnken design and observed responses

Run	Liquid to solid ratio A(g/mL)	Factor Extraction Temperature B(°C)	Extraction Time C(h)	Response Absorbance
1	12	4	71	0.258
2	12	4.5	74	0.276
3	14	4	74	0.382
4	16	4	71	0.267
5	12	3.5	74	0.217
6	16	4.5	74	0.235
7	14	4	74	0.394
8	12	4	77	0.265
9	16	4	77	0.259
10	14	3.5	71	0.253
11	16	3.5	74	0.234
12	14	4.5	77	0.314
13	14	3.5	77	0.275
14	14	4	74	0.39
15	14	4	74	0.387
16	14	4	74	0.385
17	14	4.5	71	0.271

Table.2. Estimated regression coefficients for the quadratic polynomial model and the analysis of variance (ANOVA) for the results of the experiment.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Significance
Model	0.063	9	7.04E-03	68.22	< 0.0001	**
A	5.51E-05	1	5.51E-05	0.53	0.4885	
B	1.71E-03	1	1.71E-03	16.59	0.0047	*
C	5.12E-04	1	5.12E-04	4.96	0.0611	
AB	8.41E-04	1	8.41E-04	8.15	0.0245	*
AC	5.63E-05	1	5.63E-05	0.55	0.4842	
BC	1.10E-04	1	1.10E-04	1.07	0.3356	
A^2	0.028	1	0.028	271.5	< 0.0001	**
B^2	0.018	1	0.018	175.42	< 0.0001	**
C^2	8.08E-03	1	8.08E-03	78.32	< 0.0001	**
Residual	7.22E-04	7	1.03E-04			
Lack of Fit	6.37E-04	3	2.12E-04	9.96	0.0251	*
Pure Error	8.52E-05	4	2.13E-05			

Cor Total	0.064	16		
R-Squared	0.9887		Adj R-Squared	0.9742
C.V. %	3.41			

Note: "**" indicates p <0.0001, "*" indicates p <0.05

Table 1 presents the design and corresponding response data of this experiment for the ACAD crude oil. The regression coefficients of the linear, intercept, quadratic and mutual influence of the model were calculated by the least square technique and are displayed in Table 2. It was obvious that three quadratic factors were significant at the level of $P < 0.05$. The coefficients of independent variables were descripted in the following equation:

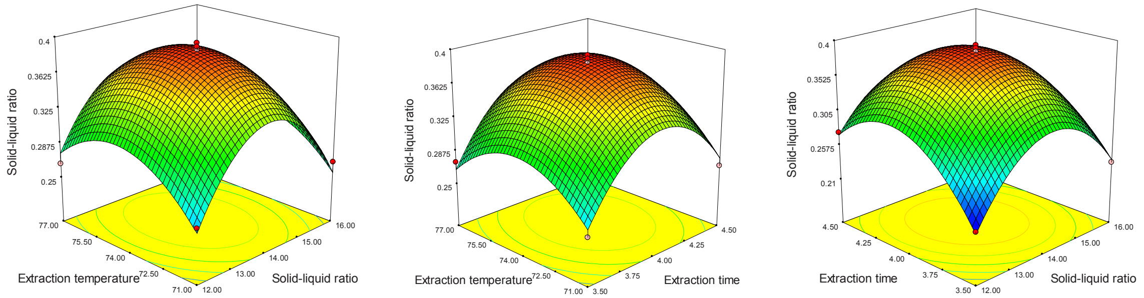
Y=-35.17288+0.67379A+2.07085B+0.71768C-0.014500AB-6.25000E-004AC+3.50000E-003BC-0.020388 A2-0.26220B2-4.86667E-003C2

Table 2 shows the variance (ANOVA) result analysis of this model. It shows a good model performance with the correlation coefficient (R2) value of 0.9887. The crude oil extraction ratio was explained by the calculated model. The statistical analysis showed a high significant level (P=0.0001), certificating a good fitness of the model in case of the crude oil extraction rate. The results indicated that the model could work better for predicting the crude oil extract from ACAD.

4.3. Analysis of response surfaces

The best method of performancing the effect of all independent variables on the crude oil extraction rate is to emerge surface response plots of the model.

Fig. 2 shows the result of interaction terms of the optimization conditions for the extraction of crude oil from ACAD. Fig. 2b and c shows the interaction of extraction temperature with each of the two other parameters on the crude oil extraction rate, respectively. As seen from Fig. 2b and c, it suggested that the extraction time was more significant than the other two effects. There was a clear optimal extraction time around 3.92 in all cases. Fig. 2a and b shows the effects of extraction temperature with each of the two other parameters on the crude oil extraction rate. The crude oil rate raised with extraction temperature rising from 71 to 72.37℃. When the temperature was more than 72.37℃, the crude oil rate seemed to go down, which indicated that the extraction temperature had obviously effect on the crude oil rate. Fig. 2a and c shows the effects of liquid-solid ratio interaction terms with each of the two other parameters on the crude oil extraction rate. It suggested that the lower yield resulted from lower solvent volume, the crude oil extraction rate raised up to a certain value with increasing liquid-solid ratio from 12:1 to 14.52:1, and then went down. As seen from Fig. 2a, b and c, the most significant factor was extraction time. The extraction rate of crude oil raised up rapidly with the extraction time increasing. It is likely that the increase in time curtails the time of mass transfer and then improves the extraction rate.



(a) (b) (c)

Fig.2. Response surface plots displaying influences of the extraction factors on extraction rate of crude oil (a) at varying extraction temperature and solid-liquid ratio, (b) at varying extraction time and extraction temperature, and (c) at varying extraction time and solid-liquid ratio,.

4.4. Optimization of the conditions

The boundary values and the extreme value obtained were analyzed with the response surface software. The optimal adsorption conditions of the crude oil extraction yield were A = 14.52, B = 72.37 and C =3.92. Taking into account the convenience of the actual operation, the optimum conditions of adsorption were amended to read as follows: solid-liquid ratio was 1:14(g/mL), extraction time was 4h and extraction temperature was 72℃. Then verified the experiment under these conditions and repeated five times. The model equation can predict the optimum response values suitability by testing the selected optimal conditions.

Table.3. The validation test of crude oil extract conditions

Test number	1	2	3	4	5
Absorbance	0.427	0.418	0.439	0.421	0.43
Average value			0.427		

4.5. The results of GC-MS

The results of GC-MS showed there were 39 kinds of compounds in which the main substance content attains a total of 11.974% and the second attains 7.661%. And the second main substance was linoleic acid. At the same time, there were oleic acid, methyl oleate, ethyl oleate, ethyl linoleate, ylangene, tetradecane aldehyde, palmitic acid, methyl hexadecanoate, ethyl hexadecanoate and some alkanes in the crude oil extraction.

5. Conclusion

In this work, the extraction of crude oil from ACAD was surveyed with a three-variable, three-level experiment designed by Box–Behnken, which was based on response surface methodology in enhancing the absorbance. The optimum extraction factors were received and the predicted values for the absorbance were well in accordance with the experiments'. The optimum conditions of Alliums cepa. L. var. agrogatum Don crude oil extraction were: extraction temperature 72℃, extraction time 4h and liquid-solid ratio 14:1.

Hyperlipidemia is a fatal factor for patients with coronary heart disease (CHD). In China, CHD has become the second factor of cardiovascular death [8]. Linoleic acid in the crude oil extraction was benefit for cardiovascular and cerebrovascular diseases [9]. So maybe the extraction of crude oil from ACAD can be developed into a kind of hypolipidemic drugs.

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Table.4. The results of GC-MS

Peak #	R.T. min	peak height	% of max.	Peak #	R.T. min	peak height	% of max.
1	11.331	37200	0.18%	**20**	20.391	204535	1.32%
2	11.948	28645	0.18%	**21**	20.436	436802	2.60%
3	12.522	47012	0.25%	**22**	20.557	813121	7.66%
4	12.88	22141	0.11%	**23**	20.627	510249	7.07%
5	13.999	32735	0.21%	**24**	20.801	847902	6.50%
6	14.165	40165	0.23%	**25**	20.875	352644	3.71%
7	15.323	85639	0.48%	**26**	21.097	220475	2.30%
8	16.411	83132	0.42%	**27**	21.325	545216	3.18%
9	16.446	169938	0.94%	**28**	21.681	226836	3.44%
10	16.556	45540	0.30%	**29**	22.035	524262	3.44%
11	17.516	241507	1.42%	**30**	22.109	2236197	11.97%
12	17.658	78050	0.62%	**31**	22.179	810247	4.76%
13	18.536	322582	1.85%	**32**	22.997	701566	4.22%
14	18.626	192953	1.08%	**33**	23.784	712355	4.45%
15	18.977	225813	2.22%	**34**	24.255	258220	2.68%
16	19.294	295762	1.86%	**35**	24.539	451868	2.55%
17	19.507	402399	2.26%	**36**	25.217	260195	2.55%
18	20.184	144871	1.12%	**37**	25.648	186056	3.37%
19	20.267	253359	1.86%	**38**	29.411	196269	3.29%
				39	29.842	96293	1.37%

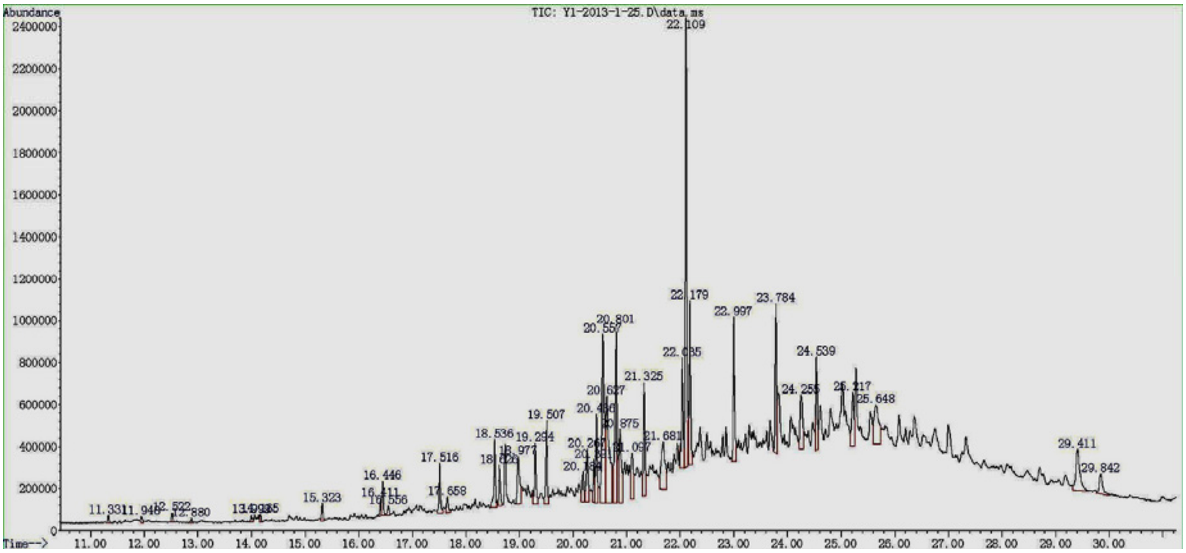

Fig.3. The results of GC-MS

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