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Optimization of preparation of calcium propionate from eggshell by Response Surface Methodology (RSM)

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Abstract

Response surface methodology (RSM) was used to investigate the preparation-process parameters on calcium propionate from eggshell. Box-Behnken was used for experimental design and the optimal combination of the preparation-process parameters for preparing calcium propionate was analyzed. Multiple regression analysis was used to fit the experimental data to the second-order polynomial equation, and appropriate statistical methods were used for analysis. The results show that optimum preparation conditions of calcium propionate were as follows: reaction temperature of 85 °C, solid-liquid ratio of 1:16, propionic acid concentration 176.00%, ultrasonic power of 135 W, ultrasonic time of 1.4 min, primary reaction time of 1.0 h and second reaction time 64.00 min. Under the optimum preparation conditions, the experimental yield of calcium propionate was 96.12%, which was in good agreement with the predicted value.

Keywords: calcium propionate; eggshell; response surface methodology.

Practical Application: Through the rational development and utilization of discarded eggshells, the purpose of turning waste into treasure has been realized.

1 Introduction

Calcium is one of the basic elements necessary for the human body. It plays an important role in the formation of bones (Fayet-Moore et al., 2019), participates in the neuromuscular stress process (Seta et al., 2004), and can also maintain the survival and function of cells (Sukumaran et al., 2016). Some scholars have conducted long-term studies on the role of calcium in the human body, and they have unanimously pointed out that people of all races are threatened by calcium deficiency throughout their lives (Balk et al., 2018; Harinarayan et al., 2021). It is difficult to get enough calcium from dietary sources, so the people do not consume calcium from dietary sources in sufficient amounts as established by the clinical guidelines (Waheed et al., 2019). Insufficient or excessive calcium in the body will affect growth and health. Insufficient calcium intake can lead to calcium deficiency, which is mainly manifested in bone diseases, such as adult osteoporosis (Mandatori et al., 2021).

In 2018, global egg production was over 76.7 million tons (Ahmed et al., 2021). Through social media we can see how people in different countries perceive eggs (Sass et al., 2020), and many factors influence consumers' perceptions of eggs and subsequent egg purchases (Sass et al., 2021). From a national perspective, China has been the world's largest egg producer for the past three decades, with total production reaching a peak of 31 million tons in 2016 (Yang et al., 2018). By-product eggshells account for about 10% of egg weight (Laca et al., 2017), leading to a large accumulation of eggshell waste (Ahmed et al., 2019). Therefore, the amount of eggshells available to us is huge. Eggshell-derived $CaCO_3$ increases the hardness value of low carbon steel composite coatings by co-deposition (Adams et al., 2022). And eggshell waste is an inexpensive source of calcium (Kumar et al., 2022). At present, calcium products used in the market are mainly derived from marine organisms and minerals. However, the content of heavy metals in eggshell raw materials and eggshell calcium products is much lower than that of marine organisms (oyster shells) and mineral sources (calcite) (Xu et al., 2020). Therefore, eggshell calcium products are safer. More than 90% of the calcium in the eggshell is $CaCO_3$, which is not easily digested and absorbed by the human body (Wallot et al., 1996). Therefore, the conversion of inorganic calcium into organic calcium is more conducive to the body's absorption. There have been previous studies on the conversion of $CaCO_3$ to calcium acetate (Yao et al., 2022), as well as calcium fortification of bread in egg shells (Khan et al., 2021; Chi et al., 2022).

Calcium propionate can be used as an antifungal agent for food, and as a preservative for bread and cakes (Belz et al., 2012). Calcium propionate is easy to mix with flour evenly, and it can provide the necessary calcium for the human body while serving as a fresh-keeping preservative, and play the role of fortifying food. Calcium propionate is a new type of food preservative developed in my country in recent years. It has stronger antiseptic ability and safer than sodium benzoate (Suhr & Nielsen, 2004).

There is no specific study on the preparation of calcium propionate from eggshells. This article hopes to use discarded eggshells to prepare calcium propionate and use Response

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surface method (RSM) to optimize the preparation conditions of calcium propionate. RSM is an effective statistical technique that uses multivariate methods to optimize complex processes (Bezerra et al., 2008). RSM is a collection of mathematical and statistical techniques widely used in the food industry to assess the relationship between independent variables and the predicted values of dependent variables (Box & Wilson, 1951). The main advantage of RSM is that it reduces the number of experiments required to evaluate multiple variables and their interactions; therefore, RSM requires less work and time compared to other methods (Wu et al., 2007). In addition to the reaction temperature, solid-liquid ratio and propionic acid concentration that need to be explored for conventional preparation. In order to make the eggshells more fully contact with propionic acid, we performed ultrasonic treatment on the eggshells for different times. Moreover, the secondary reaction method used in the process of preparing calcium propionate, which could greatly promote the reaction between eggshells and propionic acid. Through the rational development and utilization of eggshells, this research achieves the purpose of turning waste into treasure, making full use of resources, and promoting sustainable economic development. Therefore, it is necessary to study the preparation of calcium propionate from eggshells.

2 Materials and methods

2.1 Materials and chemical reagents

The eggshells were obtained from those commercial eggs. Distilled water came from the laboratory. Propionic acid were purchased from Jilin Jintai Chemical Glass Co., Ltd.

2.2 Preparation of calcium propionate from eggshells

Weigh the eggshell powder separated by the shell membrane. At a certain temperature (20, 40, 60, 80 and 100 °C), different volumes of distilled water (solid-liquid ratio 1:4, 1:8, 1:12, 1:16, 1:20, 1:24, 1:28 and 1:32), different concentrations of propionic acid (100%, 120%, 140%, 160%, 180% and 200%), different ultrasonic power(50, 100, 150, 200, 250 and 300 W), different ultrasonic time(1, 2, 3, 4, 5 and 6 min) were added to the eggshell powder. And at the same time, soybean oil was added as defoamer for neutralization reaction. In order to make the eggshell powder reaction complete, the secondary reaction method was required. After different primary reaction times (0.5, 1, 1.5, 2, 2.5 and 3 h), propionic acid with different concentrations were added for the second reaction with different reaction times (0, 20, 40, 60, 80 and 100 min). Then the yield of calcium propionate was calculated as Equation 1.

$$\text{Calcium citrate yeild} = \frac{m_1}{m_2} \times 100\% \tag{1}$$

where m_1 is the actual yield of calcium propionate, g; m_2 is the theoretical yield, g.

2.3 Optimization design and statistical analysis of calcium propionate

First, the preliminary range of the optimized variables for preparing calcium propionate was determined by single factor experiments. Then, the preparation parameters were optimized by RSM. To determine the comprehensive influence of independent variables on the reaction, a Box-Behnken design with seven independent variables at three levels was designed using Design-Expert.V8.0.6 statistical analysis software.

3 Results and discussion

3.1 Single factor experiment results

Effect of temperature on the yield of calcium propionate

The effect of temperature on the yield of calcium propionate was shown in Figure 1a. The preparation of calcium propionate was carried out at different temperatures (20, 40, 60, 80 and 100 °C). Other conditions were: solid-liquid ratio of 1:12, propionic acid concentration of 160% (theoretical dosage is 100%), ultrasonic power of 150 W, ultrasonic time of 3 min, primary reaction time of 1.5 h, secondary reaction time of 20 min. It can be seen from the figure that when the temperature reaches 80 °C, the yield of calcium propionate was the highest (89.8%).The increase of reaction temperature would increase the number of activated molecules and the effective collision between molecules, leading to the increase of the yield of calcium propionate. However, when the reaction temperature exceeds 80 °C, the yield of calcium propionate decreased. This is mainly because the higher the temperature, the faster the propionic acid volatilizes. Therefore, 80 °C was the best temperature for the production of calcium propionate.

Effect of solid-liquid ratio on the yield of calcium propionate

The effect of solid-liquid ratio on the yield of calcium propionate was shown in Figure 1b. The solid-liquid ratio was set at 1:4, 1:8, 1:12, 1:16, 1:20, 1: 24, 1:28 and 1:32, respectively; other invariable conditions were as follows: reaction temperature 80 °C, propionic acid concentration 160%, ultrasonic power 150 W, ultrasonic time 3min, one reaction time 1.5h and secondary reaction time 20min. As the solid-liquid ratio increased, the yield of calcium propionate also increased significantly. The yield reached its peak when the solid-liquid ratio was 1:16 (91.8%). Then the yield gradually decreased as the solid-liquid ratio increased. The reason for this phenomenon may be that the solid-to-liquid ratio was too low, and the reaction between the eggshell and propionic acid was incomplete. While too high would cause dilution of propionic acid and affect the yield of calcium propionate.

Effect of propionic acid concentration on the yield of calcium propionate

To investigate the effect of propionic acid concentration on the yield of calcium propionate, the process was carried out with different concentrations of propionic acid: 100%, 120%, 140%, 160%, 180% and 200% (theoretical value is 100%). Other parameters were set as follow: reaction temperature of 80 °C,

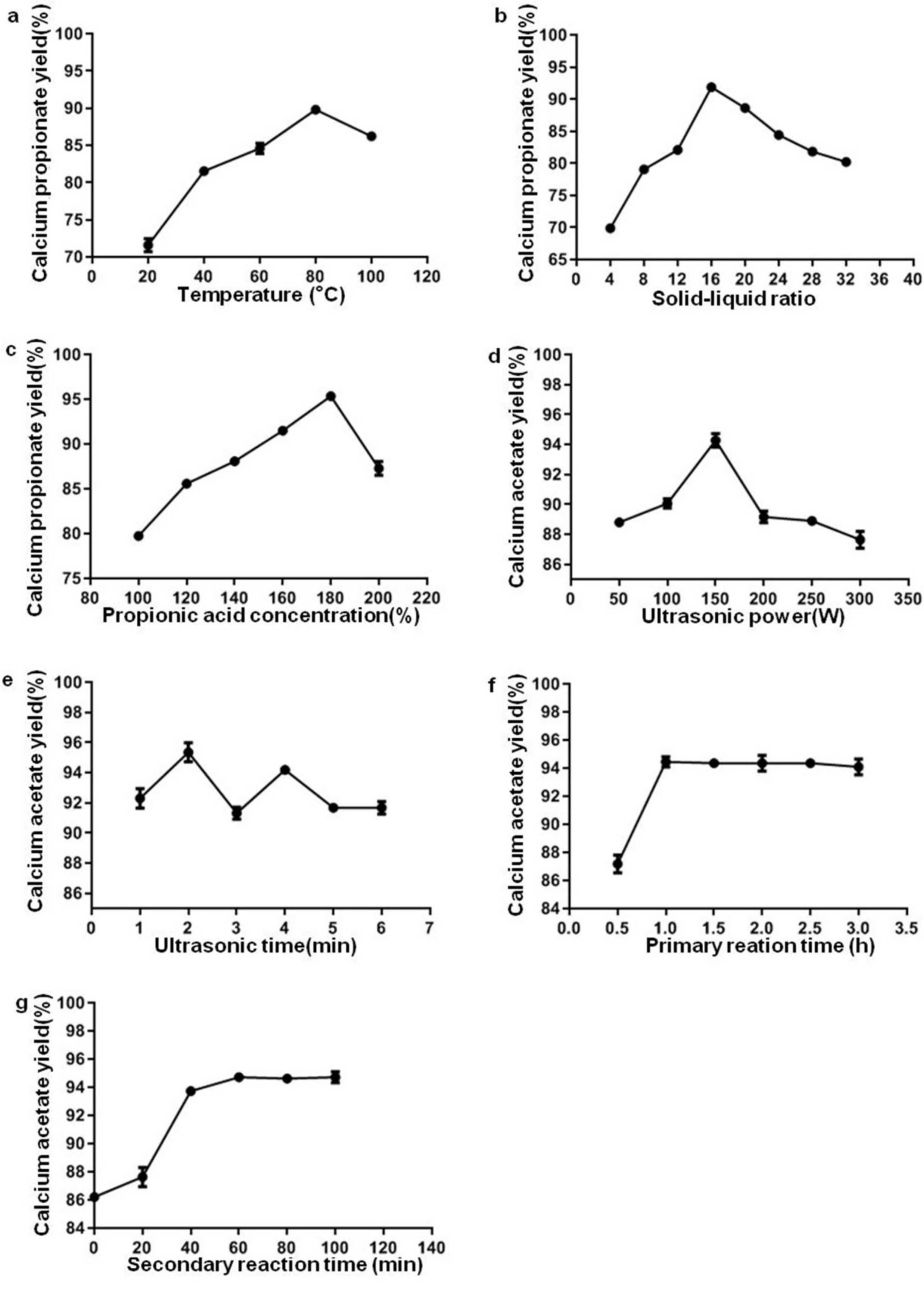

Figure 1. Effects of different (a) temperature, (b) solid-liquid ratio, (c) propionic acid concentration, (d) ultrasonic power, (e) ultrasonic time, (f) primary reaction time, (g) secondary reaction time on preparation of calcium propionate from eggshell.

solid-liquid ratio of 1:16, ultrasonic power of 150 W, ultrasonic time of 3 min, primary reaction time of 1.5 h, and secondary reaction time of 20 min. As shown in Figure 1c, with the increase of the amount of propionic acid, the yield firstly increases. Sufficient amount of propionic acid can make the reaction more fully. When the concentration of propionic acid was 180%, the yield of calcium propionate reached the maximum (95.3%). Subsequent yields decrease as the amount of propionic acid increases. Therefore, 180% was selected as the propionic acid for the preparing calcium propionate from eggshells.

Effect of ultrasonic power on the yield of calcium propionate

The effect of ultrasonic power on the yield of calcium propionate was shown in Figure 1d. The preparations were carried out at different ultrasonic power (50, 100, 150, 200, 250 and 300 W), whilst conditions were set as follows: reaction temperature 80 °C, solid-liquid ratio of 1:16, propionic acid concentration of 160%, ultrasonic time of 3 min, primary reaction time of 1.5 h and secondary reaction time 20 min. The yield increased with increasing ultrasonic power, reaching a peak at 150W (94.3%). Thus, 150 W was the best ultrasonic power for the preparation of calcium propionate. Utilize the violent vibration and cavitation of ultrasonic waves to accelerate the movement of molecules, promote the reaction of eggshells with organic acids and the formation of product crystals, shorten the reaction time, and increase the conversion rate of eggshells.

Effect of ultrasonic time on the yield of calcium propionate preparation

The effect of ultrasonic time on the yield of calcium propionate prepared from eggshells was shown in Figure 1e. Calcium propionate was under different ultrasonic times (1 min, 2 min, 3 min, 4 min, 5 min, 6 min) when other preparation parameters were set as follows: reaction temperature of 80 °C, solid-liquid ratio of 1:16, propionic acid concentration of 160%, ultrasonic power of 150 W, primary reaction time of 1.5 h and secondary reaction time of 20 min. The results showed that the calcium propionate yield was the highest when the ultrasonic time was 2 min. Therefore, 2 min was selected as the ultrasonic time for futher experiments.

Effect of primary reaction time on the yield of calcium propionate

The effect of primary reaction time on the yield of calcium propionate prepared from eggshells was shown in Figure 1f. Preparation of calcium propionate was carried out under different primary reaction time (0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h). And control other conditions were reaction temperature of 80 °C, solid-liquid ratio of 1:16, propionic acid concentration of 160%, ultrasonic power of 150 W, ultrasonic time of 2 min, secondary reaction time of 20 min. with the increase of reaction time The yield reached a peak at peaking at primary reaction time of 1.0 h (94.4%), followed by a slight decrease. The reaction completely required sufficient time. However, when the reaction time was too long, the re-dissolution reaction occurred, resulted in a decrease in the yield of calcium propionate. Therefore, 1 h was sufficient to obtain maximum calcium propionate.

Effect of secondary reaction time on the yield of calcium propionate

The effect of calcium propionate on the yield of calcium propionate was shown in Figure 1g. The secondary reaction time was set at 0, 20, 40, 60, 80 and 100 min. Other experimental conditions were as follows: reaction temperature of 80 °C, solid-liquid ratio of 1:16, propionic acid concentration 160%, ultrasonic power of 150 W, ultrasonic time of 2 min, primary reaction time of 1.0 h. With the increase of the secondary reaction time, the yield of calcium propionate increased, and the yield peaked at 60 min (94.7%) and then stabilized. The low yield with secondary reaction time of 0 min indicated that only primary reaction cannot fully react the eggshell with propionic acid, confirming the necessity of the second reaction.

3.2 Optimization of Calcium Propionate Preparation

Model fitting

The range of five independent variables was based on the results of the single-factor experiments. A total of 62 runs for seven variables to optimize the preparation of calcium propionate from eggshells (A, reaction temperature, B, solid-liquid ratio, C, propionic acid concentration, D, ultrasonic power, E,ultrasonic time, F, primary reaction time, G, secondary reaction time) in the current Box-Behnken design were shown in Table 1.

The results indicated that the maximum yield of calcium propionate was 95.9% under the preparation conditions of temperature of 80 °C, solid-liquid ratio of 1:16, propionic acid concentration of 180%, ultrasonic power of 150 W, ultrasonic time of 2 min, primary reaction time of 1 h, and secondary reaction time of 60 min. The first step of optimization was to determine the appropriate model regression to match the experimental data based on the Box-Behnken design (Aslan & Cebeci, 2007; Souza et al., 2005). Based on the Box-Behnken experimental design model, through multiple regression analysis of the experimental data, the response variables and the test variables were correlated according to the following second-order polynomial equation, Equation 2.

$$\begin{aligned} Y = {} & +95.65+1.08\times A+0.60\times B-0.53\times C-1.09\times D-0.85\times E+0.92\times F+0.78\times G- \\ & 0.52\times AB+0.23\times AC+0.35\times AD-0.39\times AG+0.55\times BD+0.24\times BE-0.16\times BF-0.34\times CD- \\ & 0.26\times CF+0.26\times DF-0.34\times EF+0.24\times EG-0.51\times FG-1.92\times A^2-1.34\times B^2-1.36\times C^2-1.36\times D^2- \\ & 0.84\times E^2-1.31\times F^2-0.91\times G^2 \end{aligned} \tag{2}$$

Where Y is the yield of calcium propionate, and A, B, C, D, E, F and G are reaction temperature, solid-liquid ratio, calcium propionate concentration, ultrasonic power, ultrasonic time, primary reaction time and secondary reaction time, respectively.

The fitting statistics of the preparation yield (Y) of the selected quadratic prediction model was shown in Table 2. The determination coefficient (R^2 = 0.9916) by analysis of variance(ANOVA) of quadratic regression model indicated that only 0.84% of the total variations were not explained by the model. However, a large value of R^2 did not imply that the regression model was good. The value of the adjusted

Table 1. The Box-Behnken design and the yield of calcium propionate.

Number	Temperature (°C)	Solid liquid ratio	Propionic acid concentration (%)	Ultrasonic power (W)	Ultrasonic time (min)	primary reaction time (h)	secondary reaction time(min)	Yield (%)
1	80	16	200	100	2	1	80	93.6
2	80	16	180	150	2	1	60	95.9
3	80	16	200	200	2	1	80	90.8
4	80	16	200	200	2	1	40	89.2
5	80	20	160	150	2	0.5	60	91.6
6	60	20	180	200	2	1	60	90.3
7	80	20	180	150	3	1	80	93.5
8	80	16	180	150	2	1	60	95.5
9	80	20	180	150	1	1	80	94
10	100	16	180	150	2	1.5	80	93.4
11	60	16	200	150	3	1	60	89.1
12	80	20	160	150	2	1.5	60	93.7
13	80	12	180	150	3	1	40	90
14	60	16	180	150	2	0.5	40	87.7
15	80	16	180	100	1	0.5	60	93.4
16	80	16	160	100	2	1	80	94
17	60	16	160	150	3	1	60	90.2
18	80	12	200	150	2	0.5	60	89.7
19	80	16	180	150	2	1	60	95.6
20	100	16	200	150	3	1	60	91.2
21	80	12	180	150	1	1	40	92.4
22	80	20	180	150	1	1	40	93.1
23	80	16	180	100	3	0.5	60	91.8
24	80	12	200	150	2	1.5	60	91.4
25	80	16	180	200	3	0.5	60	89.5
26	100	20	180	100	2	1	60	92.5
27	80	16	160	100	2	1	40	92.7
28	100	20	180	200	2	1	60	91.8
29	80	16	160	200	2	1	40	91.1
30	60	16	200	150	1	1	60	90.2
31	80	12	160	150	2	1.5	60	93.1
32	100	16	200	150	1	1	60	93.4
33	80	20	180	150	3	1	40	91.8
34	100	12	180	200	2	1	60	90.6
35	80	16	180	200	3	1.5	60	90.7
36	100	12	180	100	2	1	60	93.2
37	80	20	200	150	2	1.5	60	92.6
38	100	16	180	150	2	0.5	40	90.9
39	80	16	180	100	1	1.5	60	94.9
40	80	16	180	200	1	0.5	60	90.5
41	80	12	160	150	2	0.5	60	89.9
42	100	16	160	150	1	1	60	93.8
43	100	16	160	150	3	1	60	92.1
44	80	16	200	100	2	1	40	92
45	80	16	180	100	3	1.5	60	92.6
46	80	20	200	150	2	0.5	60	91.1
47	80	12	180	150	3	1	80	92.2
48	80	16	160	200	2	1	80	92.7
49	60	16	180	150	2	0.5	80	91.2
50	100	16	180	150	2	1.5	40	93.5
51	80	16	180	150	2	1	60	95.6
52	60	20	180	100	2	1	60	92.1
53	100	16	180	150	2	0.5	80	92.8
54	60	12	180	100	2	1	60	91
55	60	16	180	150	2	1.5	80	92
56	80	16	180	150	2	1	60	95.7
57	60	16	160	150	1	1	60	92.2
58	80	16	180	200	1	1.5	60	93.7
59	60	16	180	150	2	1.5	40	90.6
60	60	12	180	200	2	1	60	86.7
61	80	16	180	150	2	1	60	95.6
62	80	12	180	150	1	1	80	93.5

Table 2. Regression coefficients of the predicted quadratic polynomial model.

Source	Sum of Squares	Degrees of freedom (df)	Mean Square	F-Value	p-value Prob > F
Model	231.47	35	6.61	99.95	< 0.0001 significant
A-temperature	27.95	1	27.95	422.40	< 0.0001
B-Solid liquid ratio	8.64	1	8.64	130.57	< 0.0001
C-Propionic acid concentration	6.83	1	6.83	103.17	< 0.0001
D-Ultrasonic power	28.60	1	28.60	432.25	< 0.0001
E-Ultrasonic time	17.34	1	17.34	262.05	< 0.0001
F-Primary reaction time	20.35	1	20.35	307.55	< 0.0001
G-Secondary reaction time	14.57	1	14.57	220.20	< 0.0001
AB	2.21	1	2.21	33.32	< 0.0001
AC	0.41	1	0.41	6.12	0.0202
AD	0.98	1	0.98	14.81	0.0007
AE	0.080	1	0.080	1.21	0.2816
AF	0.031	1	0.031	0.47	0.4980
AG	1.20	1	1.20	18.15	0.0002
BC	0.011	1	0.011	0.17	0.6835
BD	2.42	1	2.42	36.57	< 0.0001
BE	0.45	1	0.45	6.82	0.0148
BF	0.21	1	0.21	3.19	0.0856
BG	0.061	1	0.061	0.93	0.3449
CD	0.91	1	0.91	13.77	0.0010
CE	0.020	1	0.020	0.30	0.5872
CF	0.55	1	0.55	8.33	0.0077
CG	0.011	1	0.011	0.17	0.6835
DE	1.250E-003	1	1.250E-003	0.019	0.8917
DF	0.55	1	0.55	8.33	0.0077
DG	0.011	1	0.011	0.17	0.6835
EF	0.91	1	0.91	13.77	0.0010
EG	0.45	1	0.45	6.82	0.0148
FG	2.10	1	2.10	31.76	< 0.0001
A2	49.81	1	49.81	752.75	< 0.0001
B2	24.23	1	24.23	366.11	< 0.0001
C2	25.14	1	25.14	379.90	< 0.0001
D2	25.14	1	25.14	379.90	< 0.0001
E2	9.52	1	9.52	143.81	< 0.0001
F2	23.11	1	23.11	349.23	< 0.0001
G2	11.14	1	11.14	168.33	< 0.0001
Residual	1.72	26	0.066		
Lack of Fit	1.63	21	0.077	4.07	0.0626 no significant
Pure Error	0.095	5	0.019		
Cor Total	233.19	61			
C.V. %	0.28				
R-Squared	0.9926				
Adj R-Squared	0.9827				

determination coefficient (Adj R^2 = 0.9850) also confirmed that the model was highly significant, which indicated the experimental value of calcium propionate yield was in good agreement with the predicted value. The results of error analysis indicated that the lack of fitting test (0.0896) was insignificant at the 95% confidence level, confirmed the validity of the model. Meanwhile, a relatively low coefficient of the variation (CV = 0.26) indicated a very high degree of precision and a highly reliable experimental values (Song et al., 2011). Therefore, the model was suitable for predictions within the experimental variables. In addition, the model P value (prob > f) was extremely low (< 0.0001), indicating that the model terms were significant.

3.3 Optimization of calcium propionate preparation

The effects of reaction temperature, solid-liquid ratio, propionic acid concentration, ultrasonic power, ultrasonic time, primary reaction time and secondary reaction time on the yield of calcium propionate were studied by response surface method. The regression model equation allowed the prediction of the effects of the seven parameters on the yield. The interaction types among the five tested variables and the relationship between responses of each variable and the experimental level were illustrated in 3D response-surface plots and 2D contour plots of the response surfaces (Liu et al., 2014). The circular contour plot indicated that the interactions between the corresponding variables were negligible, while an elliptical contour plot was the opposite (Muralidhar et al., 2001).

Figure 2a-f showed the three-dimensional (3D) graphic surface and contour plot of the comprehensive effects of reaction temperature and solid-liquid ratio, reaction temperature and propionic acid concentration, reaction temperature and ultrasonic power, reaction temperature and ultrasonic time, reaction temperature and primary reaction time, reaction temperature and secondary reaction time on the yield of calcium propionate. It can be seen from the figure that with the increase of various factors, the yields tend to increase first and then decrease. The central points of each factor were: temperature of 76 °C-92 °C, solid-liquid ratio of 1:14-1:18, propionic acid concentration of 160%-184%, ultrasonic power of 100w-150w, ultrasonic time of 1.5 min-2.5 min, primary reaction time of 0.9 h-1.5 h, and secondary reaction time of 56 min-80 min. The center of the contour line of Figure 2a-c and Figure 2e are elliptical. The shape was relatively dense and the surface was steep, indicating that the interaction between the two factors was obvious. The surface in the center of the contour plots of Figure 2d and Figure 2f were relatively flat, but it also forms an ellipse. It can be seen that the interaction between the various factors were obvious.

The effect of solid-liquid ratio and propionic acid concentration, solid-liquid ratio and ultrasonic power, solid-liquid ratio and ultrasonic time, solid-liquid ratio and primary reaction time, solid-liquid ratio and secondary reaction time on the yield of calcium propionate were shown in Figure 2g-k. With the increase of various factors, the yield first appeared to increase the peak value (temperature of 76 °C-92 °C, solid-liquid ratio of 1:14-1:18, propionic acid concentration of 160%-184%, ultrasonic power of 100w-150w, ultrasonic time of 1.5 min-2.5 min, primary reaction time of 0.9 h-1.5 h, and secondary reaction time of 56 min-80 min), and then decreased with the increased of various factors. The center-line area of Figure 2g and Figure 2h were elliptical, relatively dense and steep, indicating that the interaction between the two was obvious. The Figure 2i-k contour plots have relatively flat center surfaces, indicating that the interaction between solid-liquid ratio and ultrasonic power, solid-liquid ratio and ultrasonic time was not as obvious as the other factors.

Figure 2l-o showed the 3D graph and contour map of the influence of propionic acid concentration and ultrasonic power, propionic acid concentration and ultrasonic time, propionic acid concentration and primary reaction time, propionic acid concentration and secondary reaction time on yield. It can be seen from the figure that the value range of the center point of each parameter was the same as above.Moreover, the center of the contour lines is denser and the curved surface was relatively steep, indicating that the corresponding effect between these two factors was obvious. The center of the Figure 2l and Figure 2n contour were elliptical, dense and the surface were steep, indicating that the interaction were obvious. And Figure 2m and Figure 2o were relatively flat.

The effect of ultrasonic power and ultrasonic time, ultrasonic power and primary reaction time, ultrasonic power and secondary reaction time on calcium propionate yield were shown in Figure 2p-r. The center of the contour lines in Figure 2q and Figure 2r was elliptical, relatively dense, and the surface was steep, indicating that the interaction between the two was obvious. The curved surface at the center of the Figure 2p contour map was relatively flat. It shows that the interaction between the two is not obvious between other factors.

Figure 2s and Figure 2t showed the effect of ultrasonic time and primary reaction time, ultrasonic time and secondary reaction time on the yield of calcium propionate preparation. It can be seen from the figure that with the increase of various factors, the yields tend to decrease slightly after a small increase. The curved surface at the center of the figure contour map was relatively flat. It shows that the interaction between the two is not obvious.

Figure 2u shows the effect of primary reaction time and secondary reaction time on the yield of calcium propionate. As the primary reaction and the secondary reaction increase, the yield increases.

3.4 Verification of calcium propionate model

In this paper, the yield of calcium propionate was optimized by studying the reaction temperature, solid-liquid ratio, propionic acid concentration, ultrasonic power, ultrasonic time, primary reaction time and secondary reaction time. According to the prediction of Box-Behnken experimental results The optimal process for determining the preparation of calcium propionate by the model was to determine the reaction temperature of 84.55 °C, solid-liquid ratio of 1:16.15, propionic acid concentration of 176.33%, ultrasonic power of 134.94w, ultrasonic time of 1.44 min, primary reaction time of 1.18 h. and secondary reaction time of 63.83min. Under the optimum conditions, the model predicted that the yield of calcium propionate was 96.4799+/-0.735. But considering the feasibility of actual operation, the selected process parameters are reaction temperature 85 °C, solid-liquid ratio 1:16, dosage of propionic acid 176.00%, primary reaction time 1.0 h, secondary reaction time 64.00min. The highest yield of calcium propionate obtained by repeating this process was 96.12%. Within the predicted value range, the model can better reflect the actual effect of calcium propionate preparations.

In the preparation process of calcium propionate, the use of ultrasound can accelerate the reaction. Because after adding ultrasound, the neutralization reaction time is greatly shortened. The primary reaction is shortened to 1 h, and the secondary reaction is shortened to 60 min, which greatly shortens the reaction cycle of the entire experiment, reduces costs, and saves time. Under different single factor conditions, a secondary reaction method is used to increase the yield. We believe that our research has

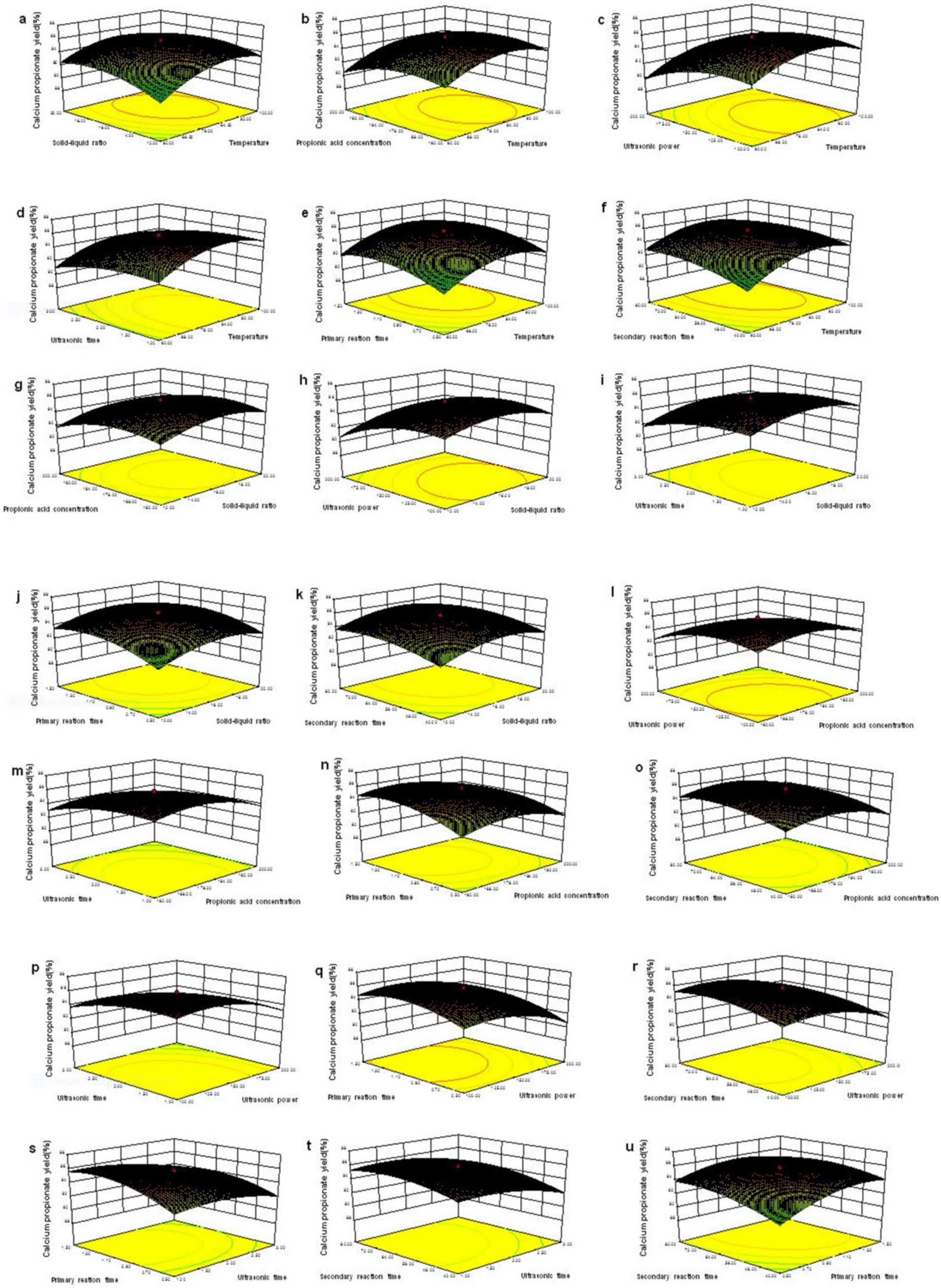

Figure 2. The effect of preparation parameters on the calcium propionate yield. (a) temperature and solid-liquid ratio, (b) temperature and propionic acid concentration, (c) temperature and ultrasonic power, (d) temperature and ultrasonic time, (e) temperature and primary reaction time, (f) temperature and secondary reaction time, (g) solid-liquid ratio and propionic acid concentration, (h) solid-liquid ratio and ultrasonic power, (i) solid-liquid ratio and ultrasonic time, (j) solid-liquid ratio and primary reaction time, (k) solid-liquid ratio and secondary reaction time, (l) propionic acid concentration and ultrasonic power, (m) propionic acid concentration and ultrasonic time, (n) propionic acid concentration and primary reaction time, (o) propionic acid concentration and secondary reaction time (p) ultrasonic power and ultrasonic time, (q) ultrasonic power and primary reaction time, (r) ultrasonic power and secondary reaction time, (s), ultrasonic time and primary reaction time (t), ultrasonic time and secondary reaction time (u) primary reaction time and secondary reaction time.

achieved the goal of turning waste into treasure, making full use of resources. And promoting sustainable economic development through the rational development and utilization of eggshells. Therefore, it is necessary to study the preparation of calcium propionate from eggshells.

4 Conclusion

In this paper, the eggshell was used as the raw material, and the RSM was used to analyze and optimize the process. Through the RSM, we determined the optimal process parameters for the preparation of c calcium propionate: reaction temperature of 85 °C, solid-liquid ratio of 1:16, propionic acid dosage of 176.00%, ultrasonic power of 135 W, ultrasonic time of 1.4 min, primary reaction time of 1.0 h, secondary reaction time of 64.00 min. Under the optimum conditions, the yield of calcium propionate could reach 96.12%. Through the rational development and utilization of eggshells, this research had achieved the goal of turning waste into treasure, made full use of resources, and promoted sustainable development of economy. Eggshell, as a new resource, needs further research in development and utilization.

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