Kinetic Analysis and Optimum Design of Extracting Pectin from Pineapple Peel by Ion Exchange

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Abstract. The pectin in pineapple peel was extracted by ion exchange method. The optimum conditions of pectin extraction were obtained by single factor and orthogonal test. Under the optimal process conditions, the kinetic model was constructed by Fick's second law, and the rate constant and apparent activation energy were obtained. The validity analysis and the model prediction ability were verified. The results show that the kinetic model can predict the kinetic process of pectin extraction from pineapple peel by ion exchange method. According to the kinetic model, the optimal conditions were obtained: the dosage of ion exchange resin was 5%, pH was 2.5, the ratio of material to liquid was 1:30 (g: mL), the extraction temperature was 85℃, the extraction time was 141.7min, and the pectin yield was 9.74%, which was consistent with the results of single factor and orthogonal test.

1. Introduction

Pectin is widely found in the cell walls of higher plants in nature. It is a kind of natural high molecular polysaccharide with galacturonic acid as the main component[1]. Pectin is often used as thickener, gelling agent, emulsifier and stabilizer in the production of food and condiment industry. Pectin is often used in the production of products, such as fruit processing, baked products, beverage production, high-quality tomato condiment[2].

Pineapple peel is the waste after people eat pineapple or industrial production of pineapple cans. A large number of pineapple peels are thrown away every year in China. If not treated in time, it will not only pollute the environment but also waste resources. The pectin content in pineapple peel is high. If it is extracted and utilized, it will improve the economic benefits of pineapple processing, which is a very meaningful research.

At present, the research on pectin in peel is mainly focused on the optimization of pectin extraction process[3,4], while the research on pectin extraction kinetic model is less[5], especially no one has studied the kinetic model of ion exchange extraction pectin. In this study, pectin was extracted from pineapple peel by ion-exchange method, and the technological conditions were optimized. On this basis, according to Fick's second law, the kinetic model of extraction process was established, and the kinetic analysis and optimization design of pectin were carried out, providing theoretical basis for production process development.

2. Materials and methods

2.1. Experimental method
2.1.1. Pretreatment of pineapple peel. Cut off the cleaned fresh pineapple peel, wash it with water, cut it into pieces, put it into a beaker, add distilled water to completely immerse the pineapple skin, soak for about 0.5h (remove impurities). Then put the beaker in the boiling water bath and boil it for about 5min. After the pectinase is eliminated in the boiling water bath, dry it in the oven. Use the high-speed grinder to crush the dried pineapple peel into powder for standby.

2.1.2. Cation exchange resin pretreatment. Cation exchange resin pretreatment: The 732 cation exchange resin was stirred in a magnetic stirrer with distilled water for 2 h, and 4 times volume of 2mol/L hydrochloric acid solution was stirred in a magnetic stirrer for 0.5h, then the resin was washed to neutral, and then 2mol/L sodium hydroxide solution was stirred in a magnetic stirrer for 0.5h, then the resin was washed to neutral, finally the 2mol/L hydrochloric acid solution was stirred in a magnetic stirrer for 3h, pour the resin out for the night, wash the resin to neutral, convert it to hydrogen resin, and put it in the oven (about 70 ℃) for drying.

2.1.3. Extraction method of pineapple pectin. 2mol/L hydrochloric acid was added to a certain volume of distilled water to prepare hydrochloric acid solution with different pH in a 250mL conical flask. Weigh 1.00g of pineapple peel powder and slowly pour it into a 250mL three port flask. Weigh a certain amount of hydrogen resin, add it to the flask, add a certain volume of hydrochloric acid solution with a certain pH, set a proper temperature, put three flasks into a water bath pot, and mix it with an electric mixer. Take down three flasks after extracting for a certain period of time, cool them at room temperature, pour them into the Buchner funnel, turn on the vacuum pump for filtration, and collect the filtrate, which is the pectin extract.

2.1.4. Drawing of galacturonic acid standard curve and calculation of pectin yield. The content of pectin was determined by carbazole colorimetry. With the concentration and absorbance of galacturonic acid as the coordinate axis, the standard working curve was drawn. The linear regression equation between galacturonic acid concentration and absorbance value is $y = 0.0075x + 0.0143$, where $y$ is the measured absorbance value, $x$ is the concentration of galacturonic acid ($\mu$L/g), $R^2 = 0.9909$.

The extraction yield $y$ of pectin is calculated as follows:

$$y = \frac{N \times V \times A}{m \times 10^6} \times 100 \quad (1)$$

Among them: pectin output is calculated by the galacturonic acid generated after hydrolysis (%); $n$ is the concentration of galacturonic acid obtained from the standard curve ($\mu$L/mL); $V$ is the volume of the extract (mL); $m$ is the mass of the peel powder (g); $A$ is the dilution times of the extract.

2.2. Kinetic model construction of pectin extraction. According to Fick's second law, a kinetic model of pectin extraction was established, with reference to. The extraction of pectin is a complicated process, which includes two steps: first, the insoluble pectin is transformed into soluble pectin, and then the soluble pectin is diffused from plant tissue to the extract. In addition, during the whole pectin extraction process, it also degrades synchronously. Let $C$ be the initial pectin concentration in pineapple peel, and the dissolution rate constant of pectin is $K_1$; the decomposition rate of soluble pectin in the extract is $K_2$; $Y(T)$ is the mass fraction of pectin in the solvent after T-Time extraction, $X(T)$ is the mass fraction of protopectin in plant tissue after T-Time extraction; $D(T)$ is the mass fraction of pectin in plant tissue after T-Time extraction; $D(T)$ is the mass fraction of pectin after T-Time degradation.

The transfer process equation of protopectin to soluble pectin is as follows:

$$\frac{dX(T)}{dT} = -K_1 \cdot X(T) \quad (2)$$

The pectin content $Y(T)$ in the extract was accumulated and decomposed at the same time:

$$\frac{dY(T)}{dT} = K_1 \cdot X(T) - K_2 \cdot Y(T) \quad (3)$$
Equation (2) and (3) occurs at the same time in practice. It needs to be combined when considering.

The integration results show that \( X(T) \), \( Y(T) \), \( D(T) \) changes with time as follows:

\[
X(T) = C \cdot e^{-K_1 \cdot T} \tag{4}
\]

\[
Y(T) = \frac{C \cdot K_1 \cdot (e^{-K_1 \cdot T} - e^{-K_2 \cdot T})}{K_2 - K_1} \tag{5}
\]

\[
D(T) = C \cdot \left(1 + \frac{K_2}{K_1} \cdot e^{-K_1 \cdot T} + \frac{K_1}{K_2} \cdot e^{-K_2 \cdot T}\right) \tag{6}
\]

\[
Y(T) = C \cdot (1 - e^{-K_1 \cdot T}) \tag{7}
\]

Equation (7) describes the theoretical situation that pectin is not degraded \((K_2=0)\), and there is no ideal situation that pectin is not degraded in reality. Therefore, it is necessary to find the time maximum \(T_{max}\) from equation (5), and the pectin content \(Y_{max}\) is the highest.

\[
T_{max} = \frac{\ln K_2}{K_1 - K_2} \tag{8}
\]

\[
Y_{max} = C \cdot \left( \frac{K_2}{K_1} \right) \cdot \left(1 - e^{-K_1 \cdot T_{max}}\right) \tag{9}
\]

The dynamic optimization parameters can be obtained from the above two formulas.

3. Results and discussion

3.1. Optimization of extraction process conditions

Accurately weigh 5 parts of pineapple peel powder, 1.00g each, respectively add different amounts of 732 type hydrogen resin (accounting for the weight of pineapple powder, the same below), extract pectin under the conditions of material liquid ratio 1:30(g:mL), pH 2.5, temperature 85℃, time 2.0h, the results are shown in Table 1.

| different amounts of 732 type hydrogen resin | % | % | % | % | % |
|---------------------------------------------|---|---|---|---|---|
| 0%                                          | 4.93 | 6.76 | 9.58 | 9.48 | 9.12 |

It can be seen from table 1 that with the addition of resin amount, the pectin yield is significantly improved, indicating that compared with the traditional acid extraction method, the ion exchange resin method has a high pectin extraction rate, and 5% resin amount is suitable. Under the condition that the resin dosage is determined, the effects of extraction temperature, pH, extraction time and ratio of extraction material to liquid on pectin extraction yield are adjusted, and the results are shown in Table 2.

| Material liquid ratio a/ (g/mL) | Yield/ % | pH b | Yield/ % | Temperature c/ ℃ | Yield/ % | t d/h | Yield/ % |
|---------------------------------|-----------|------|-----------|-------------------|-----------|------|-----------|
| 1:10                            | 5.42      | 1    | 4.23      | 70                | 5.33      | 1    | 7.65      |
| 1:20                            | 8.02      | 1.5  | 4.32      | 80                | 7.25      | 1.5  | 9.08      |
| 1:30                            | 9.58      | 2    | 9.18      | 85                | 9.58      | 2    | 9.58      |
| 1:40                            | 7.50      | 2.5  | 9.58      | 90                | 7.75      | 2.5  | 9.72      |
| 1:50                            | 5.25      | 3    | 6.58      | 95                | 4.90      | 3    | 9.48      |

a: The extraction temperature 85℃, pH value 2.5, the extraction time 2.0 h. b: The extraction temperature 85℃, the extraction time 2.0 h, the ratio of material to extraction solution 1: 30(g:mL). c: pH value 2.5, the extraction time 2.0 h, the ratio of material to extraction solution 1: 30(g:mL).
d: The extraction temperature 85℃, pH value 2.5, the ratio of material to extraction solution 1:30(g:mL).

On the basis of single factor experiment, L9 (34) was designed as orthogonal experiment to optimize the technological parameters of extracting pectin from pineapple peel. See Table 3. for experimental data and processing results. It can be seen from Table 3. that R (material liquid ratio) > R (pH value) > R (extraction time) > R (extraction temperature), indicating that the order of influence of 4 factors on pectin yield is: material liquid ratio > pH value > extraction time > extraction temperature. The optimum conditions are pH 2.5, temperature 85 ℃, time 2.5h and ratio of material to liquid 1:30 (g:mL). Under these conditions, pectin extraction rate can reach 9.72%.

Table 3. Results of orthogonal test and range analysis

| No | Material liquid ratio / (g/mL) | Temperature/℃ | pH | t/h | Yield/% |
|----|-------------------------------|---------------|-----|-----|---------|
| 1  | 1:20                          | 80.0          | 1.5 | 2.0 | 3.12    |
| 2  | 1:20                          | 85.0          | 2.0 | 2.5 | 4.92    |
| 3  | 1:20                          | 90.0          | 2.5 | 3.0 | 5.56    |
| 4  | 1:30                          | 80.0          | 2.0 | 3.0 | 6.44    |
| 5  | 1:30                          | 85.0          | 2.5 | 2.0 | 9.58    |
| 6  | 1:30                          | 90.0          | 1.5 | 2.5 | 8.74    |
| 7  | 1:40                          | 80.0          | 2.5 | 2.5 | 6.20    |
| 8  | 1:40                          | 85.0          | 1.5 | 3.0 | 4.52    |
| 9  | 1:40                          | 90.0          | 2.0 | 2.0 | 4.12    |
| k1 | 4.533                         | 5.253         | 5.460| 5.620|
| k2 | 8.253                         | 6.340         | 5.173| 6.620|
| k3 | 4.960                         | 6.153         | 7.113| 5.507|
| R  | 3.720                         | 1.087         | 1.940| 1.113|

3.2. Dynamic model

3.2.1. Effect of different extraction temperature (70℃, 80℃, 85℃, 90℃) on pectin yield and determination of model parameters. Under the condition of pH 2.0 and the ratio of material to liquid 1:30 (g:mL), the effect of different extraction temperature (70℃, 80℃, 85℃, 90℃) on pectin yield was studied, as shown in Figure 1. Using Fick's second law, the kinetic model is built, and the parameters are calculated by SPSS software to obtain the dissolution rate K1, degradation rate K2, the best time Tmax and the best yield Ymax. The calculation results are shown in Table 4. below. And the best extraction time and yield of the data obtained at 85 ℃ in Table 4. are consistent with the results of the optimal process conditions of the orthogonal design.

Table 4. Kinetic model parameters of pectin extraction from pineapple peel

| Temperature/℃ | K1×10⁴S⁻¹ | K2×10⁵S⁻¹ | T_max/min | Y_max/% |
|----------------|------------|------------|-----------|---------|
| 70             | 1.48       | 8.79       | 144.5     | 5.46    |
| 80             | 1.99       | 6.73       | 137.3     | 7.35    |
| 85             | 2.21       | 5.31       | 141.7     | 9.74    |
| 90             | 2.55       | 4.03       | 143.2     | 7.78    |

3.2.2. Validation of model parameters. The validity of the above dynamic model is analyzed, and the theoretical value and experimental data are analyzed - residual analysis and F-test. It can be seen from table 5. that with the extension of pectin extraction time in pineapple peel, there is no significant deviation to zero system and no tendency of positive and negative system in the residual error obtained from the experiment, which shows that the dynamic model obtained from the analysis of experimental
results to describe the pectin extraction process in pineapple peel is established\cite{7,8}. From the coefficient $r$ of F test, the confidence degree of the discrete data is over 99%.

| No | $t$/min | 70$^\circ$C | 80$^\circ$C | 85$^\circ$C | 90$^\circ$C | Residual |
|----|---------|-------------|-------------|-------------|-------------|-----------|
| 1  | 10      | -0.180      | 0.078       | 0.123       | -0.051      | 0.078     |
| 2  | 20      | -0.037      | -0.139      | 0.126       | -0.056      | 0.139     |
| 3  | 30      | 0.004       | 0.012       | -0.138      | 0.037       | 0.138     |
| 4  | 40      | 0.011       | 0.188       | -0.024      | 0.076       | 0.188     |
| 5  | 50      | 0.022       | -0.082      | -0.209      | -0.015      | 0.082     |
| 6  | 60      | 0.018       | -0.125      | 0.111       | -0.071      | 0.125     |
| 7  | 70      | 0.030       | -0.019      | 0.034       | 0.129       | 0.019     |
| 8  | 80      | 0.038       | 0.174       | 0.010       | -0.113      | 0.174     |
| 9  | 90      | 0.005       | 0.030       | 0.074       | -0.030      | 0.030     |
| 10 | 100     | 0.015       | 0.008       | 0.079       | 0.013       | 0.008     |
| 11 | 110     | 0.001       | -0.101      | -0.026      | 0.027       | 0.101     |
| 12 | 120     | -0.052      | -0.056      | -0.054      | 0.062       | 0.052     |
| 13 | 130     | -0.020      | -0.035      | -0.033      | -0.030      | 0.020     |
| 14 | 140     | -0.006      | -0.003      | 0.038       | 0.014       | 0.003     |
| 15 | 150     | 0.036       | 0.042       | -0.009      | 0.029       | 0.042     |
| 16 | 160     | 0.001       | 0.037       | 0.000       | -0.061      | 0.037     |
| 17 | 180     | -0.061      | 0.014       | -0.016      | -0.040      | 0.014     |
| 18 | 200     | 0.008       | 0.021       | -0.048      | 0.040       | 0.021     |
| 19 | 240     | 0.029       | -0.027      | 0.041       | 0.002       | -0.027    |
| r  |         | 0.996       | 0.995       | 0.995       | 0.998       |           |

3.2.3. Model prediction ability verification. According to the residual analysis and F test in Table 5., the model is effective. At different temperatures (70$^\circ$C, 80$^\circ$C, 85$^\circ$C, 90$^\circ$C), the measured value of pectin yield test and the calculated value predicted by the model were compared, and the results are shown in Figure 2.. At the same time, the curves of pectin content and pectin degradation with time under the optimal extraction temperature of 85$^\circ$C are listed. From Figure 2., it can be seen that the measured value of the test is in good agreement with the predicted value of the model. Therefore, the kinetic model based on Fick's second law can predict the kinetic process of pectin extraction. Using this model, the obtained kinetic rate parameters can provide theoretical support for the production and development of pineapple peel to a certain extent.

![Figure 1. Effects of different extraction temperature on pectin yield](image1.png)

![Figure 2. Fitting curve of dynamics equation](image2.png)
3.2.4. **Apparent activation energy.** The regression equation\(^9\) is obtained from the kinetic parameter \(K_1\) in Table 4. The equation is \(\ln k_1 = -3346*(1/T) + 0.9407\), \(R^2=0.9974\). The activation energy \(E_a = 27.82\text{kJ/mol}\) obtained from Arrhenius formula is significantly lower than that of the traditional extraction method without resin. The lower the activation energy, the easier the reaction. It is significant to study the kinetics and activation energy of the extraction process, to the large-scale processing of pectin extraction and the production control of corresponding products\(^10\).

4. **Conclusion**

(1) The optimum conditions of pectin extraction were obtained by single factor and orthogonal test. The amount of ion exchange resin was 5%, pH was 2.5, extraction temperature was 85 ℃, extraction time was 2.5h, and the ratio of material to liquid was 1:30 (g: mL). The pectin yield was 9.72%.

(2) The dynamic model constructed by Fick's second law was used to analyze the validity and verify the prediction ability of the model. The results show that the dynamic model can better predict the extraction process of pectin from pineapple peel by ion exchange method and provide theoretical basis for production process development.

(3) According to the kinetic parameters of the model, \(T_{max}=141.7\text{min}, Y_{max}=9.74\%\) at the extraction temperature of 85 ℃, which is consistent with the results of single factor and orthogonal test.

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