A kinetic Model of Flavonoid from Spina Gleditsiae by Supercritical CO₂ Fluid Extraction

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Abstract: A kinetic model of flavonoid from spina gleditsiae by supercritical CO₂ fluid extraction was developed by an adsorption-desorption equilibrium model. Extraction kinetic curves were fitted by origin mathematical software, and then used for prediction and experimental verification. The results showed that the prediction were consistent with the experimental process. This model illustrates solution-mass transfer mechanism of flavonoid from spina gleditsiae in supercritical extraction process, and has the advantage not only for better precision it offers, but also for the fact that it only requires moderate experimental conditions.

1. Introduction
According to the mass transfer process of the supercritical CO₂ fluid extraction for flavonoid from spina gleditsiae, and combining with the characteristics of Chinese spina gleditsiae plant matrix structure, we predicted an adsorption-desorption equilibrium in the capillary pore of spina gleditsiae, so a mass transfer model of spina gleditsiae in supercritical CO₂ fluid extraction was proposed. Based on this model, origin mathematical software was used to simulate and optimize the extraction process.

2. Materials and Methods
Spina gleditsiae were dried 2h at 105°C in oven thermostat firstly. Then they were crushed into granules, and the 60-80 mesh particles were selected for study by standard sieve. 5.0g spina gleditsiae granules above were added to 100mL extraction tank. Finally, supercritical CO₂ fluid extraction was carried out under the different conditions which used 75% ethanol as cosolvent.

3. Establishment of dynamic model
3.1. Extraction mechanism
Based on the adsorption theory and the characteristics of supercritical fluid extraction of natural products, spina gleditsiae flavonoid extraction by supercritical CO₂ extraction process is composed of the following steps: The supercritical fluid form a laminar flow on the outer surface of spina gleditsiae and then diffuse into the granule; Flavonoid molecules diffuse from the solid particles into the capillary pores inside the particles and then enter the supercritical fluid through desorption; Flavonoid molecules diffuse into the surface of granule in the capillary pore of raw material; Flavonoid molecules pass through the supercritical fluid film on the particle surface and enter the supercritical
phase; Flavonoid molecules diffuse in the supercritical fluid and be carried out from the extractor by supercritical fluid.

3.2. Assumptions in the model
Many factors influence the extraction process. There were the following assumptions according to the view of broken-complete cell structure: (i) Spina gleditsiae granule was a porous sphere after dried and crushed, and which particle porosity was $\alpha$; (ii) The molecular behavior of flavonoid was similar during extraction, and different flavonoid were assumed to be single components, and the model was suitable for each individual flavonoid; (iii) The supercritical extraction was isobaric extraction process; (iv) The fixed bed temperature of material particles was constant and the temperature gradient of the extraction bed was ignored; (v) The flow rate of fluid were consistent everywhere in the extractor; (vi) The extraction bed layer did not change during extraction, and the interstitial rate of the bed layer remains unchanged; (vii) The supercritical fluid flowing through the extractor was a continuous medium; (viii) The solute concentration in supercritical fluid was a function of time and tower height, and there was no concentration gradient in the radial direction; (ix) The length-diameter ratio of the extractor was $L/d=10.2$, and axial diffusion was ignored.

3.3. Modelling
Based on the above hypothesis, the differential equation of concentration to time of solute in supercritical fluid is as follows.

$$\frac{\alpha}{\tau} \frac{\partial c}{\partial t} + \xi = -(1 - \alpha) k_p a_p (c - c_i)$$

The differential equation of mass conservation of solute concentration in particles is as follows.

$$\beta \frac{\partial c_i}{\partial t} = k_p a_p (c - c_i) - (1 - \beta) \frac{dc_s}{dt}$$

Assuming that the desorption process is linearly reversible, and the adsorption rate is as follows:

$$\frac{dc_s}{dt} = K \frac{dc_i}{dt}$$

The boundary conditions and initial conditions are as follows.

$$t = 0, c = 0$$
$$t = 0, c_i = c_{i0}$$
$$t = 0, c_s = c_{s0}$$

$$r = R, D_e \frac{dc_i}{dr} = k_f [c - c_i (R)]$$

$$c_0 = \beta c_{i0} + (1 - \beta) c_{s0}$$

$\alpha$ is extraction bed void fraction. $c$ is the concentration of solute in supercritical fluid. $k_p$ is total mass transfer coefficient. $a_p$ is particle specific surface area., $a_p$ is $3/R$ for the spherical particles. $c_i$ is solute equilibrium concentration of particles hole. $\beta$ is the granule porosity.

3.4. Parameter estimation
In order to get mixed supercritical fluid physical parameters, the study used Kay mixing rule and the blend virtual critical parameters of the supercritical fluid was introduced into the calculation equation of the properties of supercritical carbon dioxide.

The supercritical fluid density was calculated by the equation proposed by Huang. The temperature range was 216-423k, and the applicable pressure was up to 310.3MPa.

The viscosity of supercritical fluid was calculated by the equation proposed by Jossi.

$$[(\mu - \mu_0)B10^7 + 1]^{1/4} = 1.0230 + 0.23364p + 0.58533p^2 + 0.40758p^3 + 0.093324p^4$$

The diffusion coefficient of solute in supercritical fluid was calculated by using the correlation formula proposed by He.

$$D_{AB} = \alpha \times 10^{-5} \left( \frac{T}{M_A} \right)^{1/2} \exp \left( -\frac{0.3887}{V_{rb} - 0.23} \right)$$

The mass transfer coefficient of solute in supercritical fluid was calculated by Tan's correlation formula.
\[
\text{Sh} = 0.38 \text{Sc}^{0.83} \text{Re}^{0.83}
\]

The other parameters: The void velocity of supercritical fluid was determined by the volumetric flow rate of supercritical fluid under experimental conditions. The bed voidage is 0.4. The oil content of spina gleditsiae was 10-15%, the water loss rate was 7.7% and the porosity was 0.2. The particle diameter was calculated by the mean square root of the diameter corresponding to the number of sieve mesh. The retention time was calculated by multiplying the volume of the extraction column and the interstitial rate of the bed layer, and then divided by volumetric velocity of the supercritical fluid.

4. Model calculation results and discussion

Adsorption-stripping model derived from the supercritical extraction of flavonoid of spina gleditsiae was used to fitting and analysis the dynamic data, such as the temperature, time, pressure and amount of entrainer extraction kinetics data.

4.1. Temperature

![Figure 1. Comparison of calculation yield curves at different temperature](image)

| No. | T(℃) | P(MPa) | d(mm) | \(K_p \times 10^5\)(m/s) | \(D_{AB} \times 10^9\)(m²/s) | \(k_f \times 10^5\)(m²/s) | K | MARD(%) |
|-----|------|--------|-------|--------------------------|---------------------------|--------------------------|---|---------|
| 1   | 30   | 30     | 0.68  | 0.107                    | 2.071                     | 60.712                   | 7.50 |
| 2   | 35   | 30     | 0.68  | 0.122                    | 2.356                     | 55.064                   | 6.13 |
| 3   | 40   | 30     | 0.68  | 0.139                    | 2.671                     | 54.553                   | 5.16 |
| 4   | 45   | 30     | 0.68  | 0.157                    | 3.017                     | 65.020                   | 6.49 |
| 5   | 50   | 30     | 0.68  | 0.176                    | 3.377                     | 82.526                   | 8.20 |

It was concluded that the model fit the experimental data well from Fig.1. The increase of temperature can enhance the ability of solute desorption and the diffusion coefficient of solute. As a result of the competition between the above two conditions, the adsorption equilibrium shown in Tab.1 constant first decreased and then increased with the increase of temperature.

4.2. Pressure

![Figure 2. Comparison of calculation yield curves at different pressures](image)
Table 2. Estimated parameters at different pressures

| No. | T(℃) | P(MPa) | d(mm) | $K_p\times10^5$(m/s) | $D_{ab}\times10^9$(m²/s) | $k_f\times10^5$(m²/s) | K | MARD(%) |
|-----|-------|--------|-------|---------------------|--------------------------|----------------------|---|---------|
| 1   | 40    | 20     | 0.68  | 0.120               | 2.302                    | 9.208                | 85.497 | 8.02    |
| 2   | 40    | 30     | 0.68  | 0.107               | 2.071                    | 8.282                | 62.757 | 7.12    |
| 3   | 40    | 40     | 0.68  | 0.097               | 1.873                    | 7.491                | 47.536 | 5.04    |

Fig. 2 showed that the increase of pressure increased the extraction rate and final yield of flavonoids. It could be seen that the density effect caused by the increase of pressure controlled the transfer process, and the adsorption equilibrium constant decreased with the increase of pressure.

4.3. Cosolvent concentrations

Figure 3. Comparison of calculation yield curves at different cosolvent concentrations

Table 3. Estimated parameters at different cosolvent concentrations

| No. | T(℃) | P(MPa) | d(mm) | $K_p\times10^5$(m/s) | $D_{ab}\times10^9$(m²/s) | $k_f\times10^5$(m²/s) | K | MARD(%) |
|-----|-------|--------|-------|---------------------|--------------------------|----------------------|---|---------|
| 1   | 40    | 30     | 0.68  | 0.118               | 2.271                    | 9.082                | 71.475 | 6.38    |
| 2   | 40    | 30     | 0.68  | 0.107               | 2.071                    | 8.282                | 59.424 | 5.07    |
| 3   | 40    | 30     | 0.68  | 0.099               | 1.913                    | 7.651                | 49.988 | 5.51    |

Fig.3 and Tab.3 showed the dosage of entrainer at 25ml, 37.5ml and 50ml respectively, which concluded that the calculated value of the model was well consistent with the experimental data, and the maximum MARD was 6.38%.

5. Conclusion

A kinetic model of flavonoid from spina gleditsiae by supercritical CO₂ fluid extraction was developed by adsorption-desorption equilibrium model, which can be used for the experimental results, the predicted a new process or new system, and to optimize the craft of the supercritical fluid extraction, the process of amplification and industrialization has a certain guiding significance.

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