

DYNAMICS DESCRIPTION AND THERMODYNAMICS ANALYSIS OF POLYSACCHARIDES EXTRACTION PROCESS FROM FOXTAIL MILLET

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Abstract: Polysaccharides was extracted from foxtail millet using hot water at the appropriate agitation rate and liquid to material ratio. The changing situations of polysaccharides mass concentration in the extraction solution with the extraction temperature and extraction time were measured. The experimental data obtained were fitted with the second-order dynamic model; the dynamic and thermodynamic parameters were calculated and analyzed. The results showed that the higher the extraction temperature, the shorter the time needed to reach the extraction equilibrium and the higher the polysaccharides equilibrium mass concentration. The extraction process of polysaccharides could be described with the second-order dynamic model. The apparent activation energy value was $44.34 \text{ kJ}\cdot\text{mol}^{-1}$. When the extraction temperature increased from 323 to 363 K, the half-life period value was shortened from 33.4 to 6.2 min, and the internal diffusion coefficient increased from 2.43×10^{-9} to $1.36\times 10^{-8} \text{ m}^2\cdot\text{min}^{-1}$. The enthalpy value and entropy value of the extraction process was 25.92 and $100.06 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ respectively, and the Gibbs free energy value were all less than zero, indicating that the extraction process was an endothermic, entropy increasing, spontaneous and irreversible process. Increasing the temperature was conducive to the process.

Keywords: *foxtail millet, polysaccharides, extraction, model, dynamics, thermodynamics*

INTRODUCTION

Foxtail millet is millet (*Setaria italica*) shelled grain; its particles are small, about 1 mm in diameter. It is the second largest millet cultivation in millet crops [1]. At present, China's foxtail millet has the largest planting area and output in the world, followed by India. It is one of the main food crops in northern China, with an annual output of millions of tons [2]. Foxtail millet is rich in nutrients, such as carbohydrates, dietary fiber, proteins and amino acids, fats and fatty acids, polyphenols, flavonoids, vitamins, carotenoid, minerals, and trace elements [3 – 5]. The experiment proved that there were also polysaccharides in foxtail millet [6].

Polysaccharides are widely found in natural plants [7 – 10]. In recent years, the research for extraction, purification and function of polysaccharides have become a hot topic because of their especial biological functions such as antioxidant [11], antihyperglycemic [12], anticoagulant [13], antitumor [14], antiinflammatory [15], it is also an immunomodulator, which can activate immune cells without toxic and side effects on normal cells [16].

Using a more accurate dynamical model to describe an extraction process can not only deeply understand the mechanism of the extraction process, but also provide the basis for controlling the extraction process and improving the extraction efficiency, as well as provide the basic parameters for the process, condition selection and equipment optimization design of large-scale production, so as to achieve the increase of efficiency and reduce of consumption [17]. There have been reports on the extraction of polysaccharides from foxtail millet [6, 18], but there are few reports on the dynamics and thermodynamics of the extraction process. The main works of this study were as follow: (1) the polysaccharides was extracted from foxtail millet by hot water; (2) the change situations of polysaccharides mass concentration in the extracting solution with extraction temperature and extraction time were investigated and at the appropriate agitation rate and liquid to material ratio (ratio of extraction solvent volume to foxtail millet mass, mL·g⁻¹); (3) the second-order dynamic model was employed to fit the data obtained; (4) the dynamic parameters, such as apparent activation energy, half-life period, inside diffusion coefficient were calculated; (5) the thermodynamic parameters, of enthalpy, entropy and Gibbs free energy were calculated and the thermodynamics analysis of the extraction process was carried out; in order to provide the reference of extraction process selection of foxtail millet polysaccharides, process equipment design and large-scale application.

MATERIALS AND METHODS

Materials, chemical reagents and instruments

Foxtail millet was purchased from Hangzhou supermarket, made in Harbin Xingli rice products CO. LTD, Harbin, China, 2019. The glucose (standard, Hefei Bomei biotechnology CO. LTD, Hefei, China), phenol (AR, Tianjin Damao chemical reagent factory, Tianjin, China), and sulfuric acid (98 %, AR, Yangzhou Huafu chemical CO. LTD, Yangzhou, China) were used to analysis the polysaccharides mass concentration. The sample was dried using DHG-9023A air circulation oven (Shanghai Fuxu

laboratory equipment factory, Shanghai, China). The extraction temperature was controlled by HWS-24 constant temperature electric water bath (Shanghai Yiheng scientific instrument CO. LTD, Shanghai, China). ESJ200-4a electronic analytical balance (Henan Brothers instrument equipment CO. LTD, Zhengzhou, China) was used to weight the sample mass. The absorbance of sample solution was measured using V-1100 visible spectrophotometer (Shanghai Meixie instrument CO. LTD, Shanghai, China). TD4A bench low speed centrifuge (Yancheng Kaite laboratory equipment CO. LTD, Yancheng, China) was used to deal with the sample solution.

Experimental method

Pretreatment of raw material

The raw material foxtail millet (about 1 mm in diameter) was put into the air circulation oven at 50 °C to constant weight, and then weighed and packed for use.

Extraction of polysaccharides

The temperature of the thermostatic water bath with water was set and it was awaited to be constant. 3.0 g of raw materials was weighted and enclosed into 250 mL of three flasks, and the water according to the liquid to material ratio was added into three flasks, and then the flask was fixed constant temperature water bath with stable temperature, the agitator blade was installed into the middle mouth of flask, the rotational speed of the agitator blade was adjusted. The vaporized water was condensed and returned by adding condenser pipe on one side of the mouth of flask, the extraction of polysaccharides was conducted. The extracting solution samples (5 mL of each sample) were taken at proper intervals, and it were rapidly cooled by water bath and centrifuged, and the supernatant was taken out, the mass concentration of polysaccharides was determined. The experiment was ended when the polysaccharides mass concentration was no longer increased or decreased.

Determination of polysaccharides content and calculation of yield and mass concentration

The mass concentration of polysaccharides in extracting solution was analyzed and determined according to the phenol-sulfuric acid method described in literature [19]. After sampling, color development and determination of solution absorbance, the mass concentration of polysaccharides was obtained by conversion using standard curve equation.

Since each sampling will reduce the volume of extracted liquid, (Equation 1) shall be used to modify the measured mass concentration [20].

$$C_n = \frac{1}{V_T} \left\{ [V_T - V_i(n-1)]C'_n + V_i \sum_{i=1}^n C_i \right\} \quad (1)$$

In equation (1), C_n is the modified mass concentration value of the n th sampling, $\text{mg}\cdot\text{mL}^{-1}$; n is the number of sampling; C'_n is the measured mass concentration value of the n th sampling, $\text{mg}\cdot\text{mL}^{-1}$; C_i is the modified mass concentration value of the i th sampling, $\text{mg}\cdot\text{mL}^{-1}$; V_T is the initial total volume of the extract, mL; V_i is the i th sampling volume, mL.

Dynamical model and parameters

The effective components were extracted from biomass materials, the substance of which was solid-liquid heterogeneous mass transfer and the process mechanism was complex. Clarifying the extraction mechanism is conducive to improving efficiency. There are many dynamical models used to describe the extraction process, and different materials and material shapes are suitable to be expressed by different models. It was assumed that the extraction of polysaccharides from foxtail millet at a certain temperature conformed to a second-order dynamic model [21, 22], namely (Equation 2).

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \tag{2}$$

In equation (2), t is the extraction time, min; C_t is the modified mass concentration of polysaccharides after sampling analysis at time of t , $\text{mg}\cdot\text{mL}^{-1}$; C_s is the equilibrium mass concentration, $\text{mg}\cdot\text{mL}^{-1}$; k is the extraction rate constant.

By integrating equation (2) with time from 0 to t and mass concentration from 0 to C_t , (Equation 3) can be obtained.

$$C_t = \frac{t}{(1/kC_s^2) + (t/C_s)} \tag{3}$$

Transform Equation 3 and rewrite it as Equation 4.

$$\frac{t}{C_t} = \frac{1}{kC_s^2} + \frac{t}{C_s} \tag{4}$$

According to equation (4), if polysaccharides extraction conforms to the second-order dynamic model, the relationship between t/C_t and t is linear. The equilibrium mass concentration C_s is obtained through the slope $1/C_s$ of the line, and the extraction rate constant k is calculated through the line intercept $1/(kC_s^2)$ and the C_s obtained, and then the extraction kinetic equation under various conditions can be obtained.

Apparent activation energy

According to the Arrhenius equation, the relationship between extraction rate constant k and extraction temperature T is shown in Equation 5 [23].

$$k = k_0 e^{-E_a/(RT)} \tag{5}$$

Where, k is the mass transfer rate constant, $\text{mL}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$; k_0 refers to the anterior factor, $\text{mL}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$; R is the gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; T is the extraction temperature, K; E_a is the apparent activation energy, $\text{J}\cdot\text{mol}^{-1}$.

Logarithm of both sides of Equation 5 is taken to obtain Equation 6:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \tag{6}$$

The apparent activation energy E_a value can be obtained by plotting $\ln k \sim 1/T$.

Half-life period

The half-life period ($t_{1/2}$) is the extraction time required when the mass concentration in the extracting solution is half of the equilibrium mass concentration [17, 24], i.e., when $t = t_{1/2}$, $C_t = C_s/2$, substitute into equation (4), and the half-life period calculation Equation 7 can be obtained.

$$t_{1/2} = \frac{1}{kC_s} \quad (7)$$

Each half-life period can be obtained by using the extraction rate constant k and the equilibrium mass concentration C_s values obtained previously at each temperature. Plot by taking the extracted temperature T as the abscissa axis and the half-life period ($t_{1/2}$) values obtained as the vertical axis, the relationship between the two can be obtained.

Internal diffusion coefficient

The internal diffusion coefficient (D_s) is an important factor affecting the mass transfer rate; its value represents the diffusion ability of a material molecule. Based on round granular material, the functional relationship between extraction rate constant k and internal diffusion coefficient D_s ($\text{m}^2 \cdot \text{min}^{-1}$) and mass transfer distance r (particle radius, m) is shown in Equation 8 [17].

$$k = \frac{\pi^2 D_s}{r^2} \quad (8)$$

According to Equation 8, the internal diffusion coefficient can be calculated from the calculated rate extraction rate constant and the known material size.

Thermomechanical analysis

When extracting process to achieve dynamic balance, the thermodynamic parameters of Gibbs free energy ΔG , enthalpy ΔH and entropy ΔS can be calculated by van't Hoff equation (seen Equation 9) [17, 25-26].

$$\ln K = \ln \left(\frac{C_s}{C_T - C_s} \right) = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (9)$$

Where, K is the equilibrium constant in the extraction process; C_s is the equilibrium mass concentration at each temperature, $\text{mg} \cdot \text{mL}^{-1}$; C_T is the maximum extraction mass concentration, $\text{mg} \cdot \text{mL}^{-1}$; ΔG is the Gibbs free energy of extraction process, $\text{kJ} \cdot \text{mol}^{-1}$; ΔH is the enthalpy of extraction process, $\text{kJ} \cdot \text{mol}^{-1}$; ΔS is entropy of extraction process, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; R is the gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T is the extraction temperature, K. According to equation (9), the equilibrium constant, Gibbs free energy, enthalpy and entropy of the extraction process can be calculated.

RESULTS AND DISCUSSION

Extraction experiments

Effect of agitation rate on polysaccharides extraction

The whole foxtail millet particle, liquid to material ratio of $25.0 \text{ mL} \cdot \text{g}^{-1}$, extraction time of 2.0 h, extraction temperature of $70.0 \text{ }^\circ\text{C}$, extraction once, the effects of agitation rate on the extraction of polysaccharides were investigated. The results were shown in Figure 1. The results in Figure 1 showed that with the increase of agitation rate, the mass concentration of polysaccharides in the extracting solution first increased and reached the highest point of $0.263 \text{ mg} \cdot \text{mL}^{-1}$ at $150 \text{ r} \cdot \text{min}^{-1}$, then the mass concentration

decreased. The reason is that the agitation promotes the transfer of polysaccharides from the liquid surrounding foxtail millet particles to the liquid body, reduces the mass concentration at the solid-liquid interface, increases the mass transfer impetus, and accelerates the extraction. However, after the agitation rate was greater than $150 \text{ r}\cdot\text{min}^{-1}$, the agitation rate was increased again, which had no obvious promotion effect. On the contrary, the polysaccharides already in the liquid phase are heated for a long time, leading to thermal decomposition, which reduces the mass concentration of polysaccharides. Therefore, $150 \text{ r}\cdot\text{min}^{-1}$ could be used as an appropriate agitation rate for polysaccharides extraction.

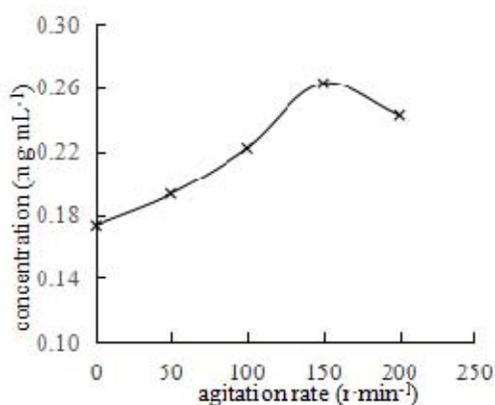


Figure 1. Effect of agitation rate on polysaccharides extraction

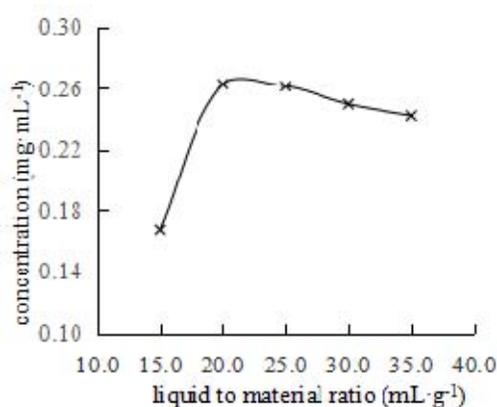


Figure 2. Effect of liquid to material ratio on polysaccharides extraction

Effect of liquid to material ratio on polysaccharides extraction

The whole foxtail millet particle, agitation rate $150 \text{ r}\cdot\text{min}^{-1}$, extraction time 2.0 h, extraction temperature $70.0 \text{ }^\circ\text{C}$, extraction once, the effects of liquid to material ratio on the extraction of polysaccharides were studied, the results were shown in Figure 2. As seen in Figure 2 that the mass concentration of polysaccharides in the extracting solution first increased with the increase of the liquid to material ratio, then peaked at the liquid to material ratio range of $20\sim 25.0 \text{ mL}\cdot\text{g}^{-1}$ and then decreased. The reason is that the mass concentration of polysaccharides in the extracting solution is decreased by increasing the liquid to material ratio, the mass transfer impetus is increased, meanwhile the viscosity of the extracting solution is decreased, and the mass transfer resistance is reduced, so the mass transfer rate is accelerated, and more polysaccharides can be extracted in the same time. However, if the liquid to material ratio is too high, the residence time of the extracted polysaccharides in the liquid phase would increase, the amount of polysaccharides degraded would increase, and the loss of polysaccharides would increase due to the increase of subsequent operation time. In addition, the operating cost will also be increased with increasing the liquid material ratio [27]. In conclusion, considering the large number of samples in the dynamic extraction experiment, the appropriate liquid to material ratio was selected to be $25.0 \text{ mL}\cdot\text{g}^{-1}$ in order to reduce the influence of volume change.

Therefore, in the dynamic extraction experiments, namely the influence test of extraction temperature and extraction time on the extraction effect, were adopted the whole foxtail millet particle, $150 \text{ r}\cdot\text{min}^{-1}$ agitation, liquid to material ratio $25.0 \text{ mL}\cdot\text{g}^{-1}$.

Effect of extraction temperature and extraction time on mass concentration of polysaccharides

Dynamic extraction experiments were carried out at extraction temperatures of 323, 333, 343, 353 and 363 K with a liquid to material ratio of 25.0 mL·g⁻¹ and an agitation rate of 150 r·min⁻¹. The relationships between the mass concentration of polysaccharides in the extracting solution and extraction time were determined at different temperature. The results were summarized in Figure 3. As seen from Figure 3, with the increase of extraction temperature, the time needed for the polysaccharides mass concentration in the extracting solution to reach the maximum value was shorter, and the corresponding equilibrium mass concentration was also relatively higher [24, 28]. This is because with the increase of temperature, the solubility of polysaccharides in the solution increases, cell wall breaking and molecular permeability increase, diffusion coefficient increases, solution viscosity decreases, then the mass transfer resistance is reduced, the mass transfer rate is accelerated, so that the polysaccharides extraction rate is speeded up and the amount is increased. But too high extraction temperature will make the polysaccharides extracted into the solution degrade and the yield reduce on account of in high temperature solution for a long time.

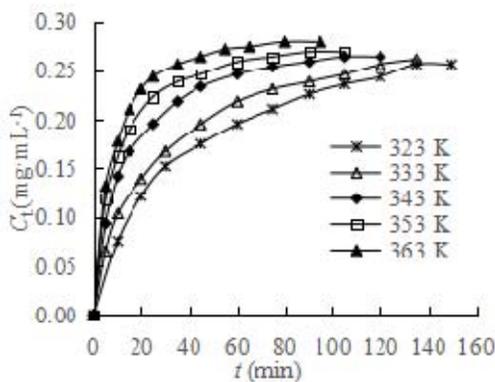


Figure 3. Relationship of C_t and t at different temperatures

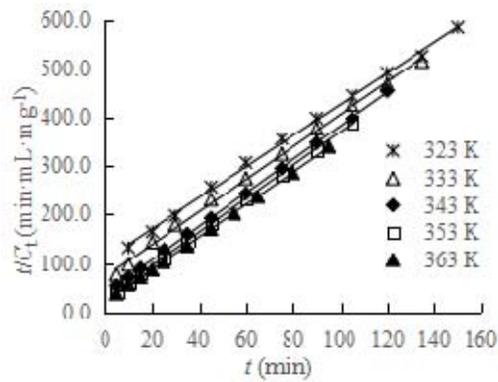


Figure 4. Relationship of t/C_t and t at different temperatures

Dynamics

Model fitting

Experimental data at different temperature were plotted as t/C_t versus t , the results were shown in Figure 4, and the model fitting results were shown in Table 1.

Table 1. The relationship fitting results of t/C_t and t at different temperatures

T [K]	Fitted equation	R^2
323	$t/C_t = 3.1965t + 106.73$	0.9979
333	$t/C_t = 3.3432t + 71.618$	0.9979
343	$t/C_t = 3.4463t + 37.759$	0.9998
353	$t/C_t = 3.4426t + 26.172$	0.9999
363	$t/C_t = 3.3316t + 20.620$	0.9998

According to the intercept and slope of the fitted line obtained by t/C_t and t diagram, C_s values and k values were calculated. The results were shown in Table 2.

Table 2. The values of rate constant k and C_s at different temperatures

T [K]	323	333	343	353	363
K [$\text{mL}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$]	0.0957	0.1561	0.3145	0.4528	0.5383
C_s [$\text{mg}\cdot\text{mL}^{-1}$]	0.3128	0.2991	0.2902	0.2905	0.3002

As seen from Figure 4 and Table 1 above, the second-order dynamic is used to fit the data measured in the experiment, and the fitting degree is very high with R^2 of linear regression coefficient of each curve greater than 0.995. The data in Table 2 shows that k value increases gradually with the increase of temperature, indicating that increasing temperature can accelerate the dissolution of polysaccharides and improve the extraction rate [28].

Apparent activation energy

The apparent activation energy E_a can be calculated by drawing $\ln k \sim 1/T$ and the results were shown in Figure 5.

As seen from Figure 5, the regression coefficient R^2 is bigger than 0.95, $\ln k$ has a good linear relationship with $1/T$, and according to the Arrhenius equation, the apparent activation energy $E_a = 44.34 \text{ kJ}\cdot\text{mol}^{-1}$ during the process of extracting foxtail millet polysaccharides by hot water at the liquid material ratio of $25.0 \text{ mL}\cdot\text{g}^{-1}$ can be calculated, which is an endothermic process [26]. Increasing the extraction temperature is conducive to the extraction of polysaccharides. The correlation is followed by $k = 1.485 \times 10^6 \exp\left(-\frac{5332.1}{T}\right)$.

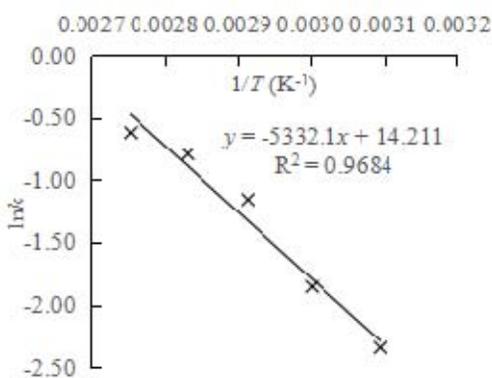


Figure 5. $\ln k$ versus $1/T$

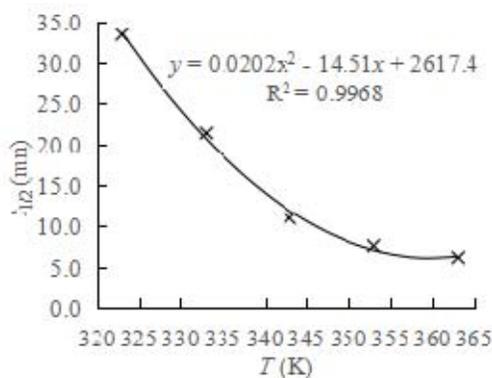


Figure 6. $t_{1/2}$ versus T

Half-life period

By substituting the value of extraction rate constant k and the equilibrium mass concentration C_s at each extraction temperature into equation (7), the value of half-life period $t_{1/2}$ at each extraction temperature can be obtained. Its value decreased from 33.4 min at 323 K to 6.2 min at 363 K. The values of $t_{1/2}$ versus T were plotted; the results were shown in Figure 6. As seen from Figure 6, the relationship between half-life period and extraction temperature can be fitted to a quadratic equation follow by

$t_{1/2} = 0.0202T^2 - 14.51T + 2617.4$; the fitting relationship is good with the regression coefficient R^2 of 0.9968. According to the fitting equation above, the time needed when the mass concentration of foxtail millet polysaccharides extracted reaches half can be calculated. As seen from Figure 6, the half-life period decreases with the increase of extraction temperature. This is because the higher the extraction temperature, the faster the extraction rate. The half-life period reflects the efficiency of extraction, the smaller the half-life period is, the faster the extraction rate of foxtail millet polysaccharides is.

Internal diffusion coefficient

The diameter of foxtail millet particles was 0.001 m and the mass transfer distance was the radius, so r was 0.0005 m. According to the extraction rate constant k at each extraction temperature, the internal diffusion coefficient D_s at each extraction temperature can be calculated according to equation (8). The figure of D_s versus T was plotted, and the results were shown in Figure 7.

The extraction temperature ranged from 323 to 363 K, and the internal diffusion coefficient ranged from $2.43 \times 10^{-9} \text{ m}^2 \cdot \text{min}^{-1}$ to $1.36 \times 10^{-8} \text{ m}^2 \cdot \text{min}^{-1}$. As the extraction temperature rises, the internal diffusion coefficient gradually increases. This reason is that the higher the extraction temperature is, the stronger the thermal motion of the molecules and the lower the viscosity of the solution are, which is conducive to the migration and diffusion of the solute. It can be seen from Figure 7 that the regression coefficient R^2 was 0.9828, showing a good linear relationship, and the correlation equation between the internal diffusion coefficient and extraction temperature was $D_s = 3 \times 10^{-10}T - 9 \times 10^{-8}$.

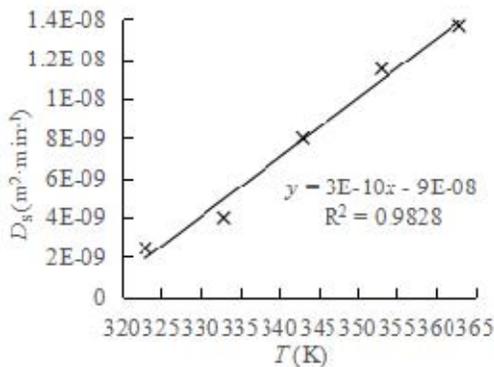


Figure 7. D_s versus T

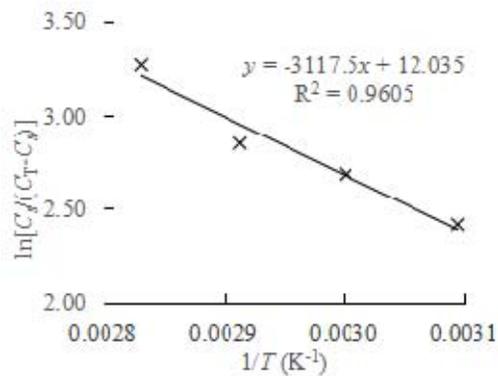


Figure 8. $\ln[C_s/(C_T - C_s)]$ versus $1/T$

Thermodynamic analysis

Under the extraction condition of water as solvent, it was assumed that the system reached the extraction equilibrium when the extraction temperature was 363 K and the extraction time was 80 min, C_s at this time was taken as C_T , that is, the intrinsic mass concentration of polysaccharides in the material under the experimental conditions. The

plot of $\ln\left(\frac{C_s}{C_T - C_s}\right)$ versus $1/T$ was drawn and the result was shown in Figure 8. The

relationship between the two was as follows $\ln\left(\frac{C_s}{C_T - C_s}\right) = -\frac{3117.5}{T} + 12.035$.

Figure 8 showed that the regression coefficient R^2 was 0.9605, showing a good linear relationship. The linear slope and intercept is $-\Delta H/R$ and $\Delta S/R$, respectively, which can calculate the values of thermodynamic parameters, enthalpy ΔH , entropy ΔS and the Gibbs free energy ΔG , the concrete values were shown in Table 3.

Table 3. Thermodynamic parameter of the extraction process

T [K]	ΔH [kJ·mol ⁻¹]	ΔS [J·mol ⁻¹ ·K ⁻¹]	ΔG [kJ·mol ⁻¹]
323	25.92	100.06	-6.40
333			-7.40
343			-8.40
353			-9.40

The value of ΔH and ΔS was 25.92 kJ·mol⁻¹ and 100.06 J·mol⁻¹·K⁻¹ respectively within the investigative range of the extraction temperature, both were greater than zero, shows that hot water extraction process of foxtail polysaccharides is a endothermal and entropy increasing process; ΔG values are all less than zero, it shows that extraction process is a spontaneous irreversible process, and ΔG value gradually decreases with the improvement of extraction temperature, and make it easier for extraction process [21, 26].

CONCLUSIONS

The experiment of extracting polysaccharides from the whole foxtail millet particle with hot water at an agitation rate of 150 r·min⁻¹ and a liquid to material ratio of 25.0 mL·g⁻¹ were implement. It was found that within the scope of the study, the extraction temperature and extraction time had a greater impact on the mass concentration of polysaccharides in the extracting solution. The equilibrium mass concentration of the extracting solution was raised and the time needed to achieve the extraction equilibrium was shortened with the raised of the extraction temperature. The extraction process can be described by the second-order dynamic model kinetic equation. The apparent activation energy of the extraction process was 44.34 kJ·mol⁻¹. The half-life period shortened as the extraction temperature increased, and the relationship between the half-life period and the extraction temperature was $t_{1/2} = 0.0202T^2 - 14.51T + 2617.4$. As the extraction temperature increased, the internal diffusion coefficient increased, and the correlation between the internal diffusion coefficient and the extraction temperature was $D_s = 3 \times 10^{-10}T - 9 \times 10^{-8}$, the ΔG value of extraction process decreased from -6.40 to -9.40 kJ·mol⁻¹, they were all less than zero, extraction process was spontaneous irreversible. ΔH value was 25.92 kJ·mol⁻¹, extraction process was endothermic. ΔS value was 100.06 J·mol⁻¹·K⁻¹, the process was entropy increasing, raising the temperature is good for the process.

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