Kinetics and Thermodynamics of Water Extraction
of Foxtail Millet Polysaccharides

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ABSTRACT: *In order to understand the mechanism of the extraction process of polysaccharides from foxtail millet by hot water, the extraction was carried out for studying the kinetics and thermodynamics of the extraction process. After the appropriate stirring rate and liquid material ratio were selected through the preliminary experiment, the changes in polysaccharides mass concentration in the extract liquor extraction temperature and extraction time were measured. The experimental data were fitted by the first-order model. The kinetics and thermodynamics parameters were calculated. The results showed that the appropriate stirring rate and the liquid material ratio were 150 r/min, 20.0 mL/g respectively. A greater extraction rate and higher equilibrium mass concentration could be obtained under higher extraction temperatures. The extraction process accorded with the first-order dynamics model. The apparent activation energy of the process was 12.03 kJ/mol under study conditions. The internal diffusion coefficient was increased with increasing temperature in the range of 7.84×10^{-10} - 1.29×10^{-9} m^2/min. The half-life was decreased from 25.2 min to 3.9 min as the temperature increased. The Gibbs free energies were all less than zero, the enthalpy change was 31.96 kJ/mol and the entropy change was 120.3 J/(mol·K) in process. The polysaccharides extraction process was a spontaneous, endothermic and entropy increases process.*

KEYWORDS: *Foxtail millet polysaccharides; Hot water extraction; Model; Kinetics; Thermodynamics.*

INTRODUCTION

Millet is a general term referring to several small-seed cereal crop species. The main millet crops are pearl millet (*Pennisetum glaucum*), foxtail millet (*Setaria italica*), proso millet (*Panicum miliaceum*), and finger millet (*Eleusine coracana*) [1]. Millet is a pseudocereal that mostly grows in the arid regions of African and Asian countries [2, 3]. In millets, foxtail millet is the second-largest millet cultivation after pearl millet [4]. Foxtail millet has a strong drought resistance and is widely planted in arid and semi-arid regions of the world [1, 5].

Foxtail millet has a high carbohydrate content which is an excellent source of energy. It is rich in carbohydrates, dietary fiber, proteins, amino acids, fats, fatty acids, polyphenols, flavonoids, vitamins, carotenoids, minerals, and trace elements such as sodium, calcium, magnesium, phosphorus, potassium, copper, iron, and selenium [1, 2, 6]. Polysaccharides are common functional components in many natural plants. In recent years, polysaccharides have attracted widespread attention because of their distinct physical and chemical properties and biological functions

such as antioxidant [7], anticoagulant [8], antihyperglycemic [9], antitumor [10], immunoregulation [11], anti-inflammatory [12], and prebiotic [13]. The polysaccharides were extracted from foxtail millet in hot water [14]. The extraction process of active components such as polysaccharides from biomass conforms to a certain law. Using a suitable mathematical model to express the dynamic process of effective component extraction can accurately explain the mechanism of the extraction process, which can be used to optimize the processes and equipment, control the extraction process, and further provide a basis for industrial applications. Therefore, it is very important to study the kinetics of the extraction process. In order to understand the effect of operating parameters on extraction kinetics, several models were proposed, which include the first-order model, the second-order model, modified Fick's law, and other empirical models [15-17]. The flavonoid concentration-time data extracted from *Terminalia bellerica* were analyzed using a second-order kinetic model to determine the extraction constant by *Krishnan* and *Rajan* (2016) [16]. The first-order, second-order, and a mass transfer model based on Fick's Law were used to correlate the overall extraction curves of soybean oil by *Dagostin et al.*(2015) [17], they pointed out that overall extraction curves were better correlated by the second-order and mass transfer models. *Toru et al.* (2015) [18] reached that the extraction data in the time course of aqueous extraction kinetics of soluble solids, phenolics, and flavonoids from sage (*Salvia fruticosa* Miller) leaves fit with the reversible first-order kinetic model. *Sant'Anna et al.* (2013) [19] found that the pseudo-first-order model provided the best description of the extraction of anthocyanins from grape marc. The study of extraction thermodynamic parameters helps to determine the possibility and extent of the extraction process. The thermodynamic research for the extraction process of *Terminalia bellerica* flavonoid [16] and soybean oil [17] showed that the extraction process is endothermic, spontaneous, and irreversible. The kinetics and thermodynamics studies of the foxtail millet polysaccharides extraction process are rarely reported in the literature. In this study, hot water was used as the extracting agent to extract polysaccharides from foxtail millet. After the preliminary experiment of a single factor, the appropriate stirring rate and liquid material ratio (water volume to foxtail millet mass ratio, mL/g) were selected. At the same time, the relationships between the polysaccharides' mass concentration in the extraction solution and extraction time at different extraction temperatures were emphatically investigated. Because foxtail millet is an approximately spherical particle, therefore the first-order kinetics model based on Fick's second Law was tried to fit the experimental data. The kinetic parameters such as apparent activation energy of extraction process, the half-life of polysaccharides mass concentration, the internal diffusion coefficient of substance molecules and the relative raffinate ratio of polysaccharides were calculated. The thermodynamics parameters such as Gibbs free energy, enthalpy change, and entropy change of the extraction process were also calculated which could provide a reference for industrial application.

EXPERIMENTAL SECTION

Materials, chemical reagents, and instruments

Foxtail millet was purchased from Hangzhou Supermarket, and 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 analyze 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 weigh the sample mass. The absorbance of the sample solution was measured using V-1100 visible spectrophotometer (Shanghai Meixie Instrument Co. Ltd, Shanghai, China). TD4A bench a 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 sample of foxtail millet (about 1 mm in diameter) was placed in an air circulation oven and dried to a constant weight of 50 ℃. At this point, the sample's moisture

determined using the oven method was 5.31% (wet matter basis). After that, the sample was weighed and packaged for use according to the experimental dosage.

Extraction of polysaccharides

The temperature of the constant temperature water bath was set. The three-necked flask and the reflux condenser were installed on the iron frame. When the water bath temperature was constant, the raw material sample weighed was taken and added to the three-necked flask. Then the water was also added to the three-necked flask according to a certain ratio of liquid to material, the polysaccharides were extracted under stirring at 150 r/min. In the preliminary experiment of a single factor investigation, the extraction operation was terminated at the scheduled time, and a sample of the extracting solution was taken and centrifuged. At last, the sample for determining was sampled from the supernatant liquor and the absorbance of the sample solution was measured. During each kinetics experiment, the sample of the extracting solution was taken, centrifuged, sampled, and analyzed at suitable intervals until the polysaccharides concentration was no longer increased or went down.

Determination of polysaccharides content and calculation of yield and mass concentration

The absorbance of the sample solution was determined by referring to the sulfuric acid-phenol method described in the references [20, 21].

The yield of polysaccharides was calculated according to the following equation (1).

$$Y = \frac{N \cdot X \cdot V}{M} \tag{1}$$

Where Y is the yield of foxtail millet polysaccharides, mg/g; N is the dilution ratio of extracting solution; V is the total volume of extracting solution, mL; X is the mass concentration of foxtail millet polysaccharides measured in the extracting solution, mg/mL; M is the dosage of raw foxtail millet in the experiment, g.

Since the samples were required to be taken at suitable intervals in each kinetics extraction experiment, the volume of the solution used to extract further will be reduced after each sampling, which will lead to the deviation of the measured mass concentration of polysaccharides, therefore the mass concentration

determined by each sampling should be calibrated according to Eq. (2) [22, 23].

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

Where C_n is the modified value of mass concentration obtained by the nth sampling analysis in mg/mL; C'_n is the mass concentration measured by the nth sampling analysis in mg/mL; n is the number of samples taken; C_i is the modified value of mass concentration obtained by the sampling analysis at ith in mg/mL. V_T is the total volume of the initial extraction solution of feeding in mL; V_i is the sample volume of the ith sampling in mL.

Experiment design

The preliminary experiment of single factor investigation was first implemented to determine the appropriate stirring rate and liquid material ratio. The relationship between the extraction mass concentration and the extraction time at different extraction temperatures was studied. Samples were sampled and analyzed; the yield and mass concentration were calculated.

Kinetics model and parameters
Kinetics model

The extraction of active ingredients from solid materials is a complicated process. Different ingredients are more or less extracted at the same time. It usually consists of three steps, that is, the solvent first penetrates into the solid material, infiltrates the material, and dissolves the active component. Next, the components dissolved in the solvent are transferred from the material to the solid-liquid interface in the form of molecular diffusion under the action of concentration difference. The effective components are finally transferred from the solid phase to the liquid phase through the interface, further in the form of molecular diffusion or convective mass transfer to the solution body [22]. In the case of mechanical agitation, the mass transfer resistance of the solid-liquid interface and from the interface to the main body of the solution can be ignored due to the forced convective mass transfer. The mass transfer resistance of the extraction process is basically concentrated in the solid phase, namely, the extraction process belongs to internal diffusion control. The active component in the material is as long as transferred to the solid surface and immediately

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transferred to the liquid phase. The liquid phase concentration is uniform. As the concentration of the active ingredient decreases with the time of extraction, the active ingredients extraction process is unstable diffusion. Considering that the material of foxtail millet particle is approximately spherical, in order to facilitate the analysis, the extraction process of extracting polysaccharides from foxtail millet at a certain temperature is tried to describe by a first-order kinetics model based on Fick's second law. A single particle is taken as the object, and it is assumed that [16, 22, 23]: (1) the particle is a homogeneous ball with radius r; (2) the mass transfer direction of the active component is along the radius direction, (3) the distribution of each component in the particle interior at the extraction initiate is uniform, (4) the mass transfer resistance on the surface of the ball is ignored and the internal diffusion coefficient of the active component remains unchanged, (5) the temperature of the particle is stable and the same as that of the solution. So the extraction process can be expressed in the following model Eq. (3) [23].

$$\frac{C^* - C_t}{C^* - C_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \exp\left[-\left(\frac{n\pi}{r}\right)^2 D_s t\right] \tag{3}$$

Where C_0 is the initial mass concentration of the active component in the extraction solution, mg/mL; C_t is the mass concentration of the active component at time t (modified value after sampling analysis, the same as below), mg/mL; C^* is the mass concentration of the active component at the extraction equilibrium, mg/mL; t is the extraction time, min; D_s is the internal diffusion coefficient, m^2/min; n is the number of terms that the function expands; r is the molecular diffusion mass transfer distance, namely, the radius, m.

The concentration distribution of unstable mass transfer is an infinite series, and the first term is usually taken when calculating. Therefore, Eq. (3) can be simplified to Eq. (4) [23].

$$\frac{C^* - C_t}{C^* - C_0} = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_s t}{r^2}\right) \tag{4}$$

Order ($k = \pi^2 D_s t / r^2$) [18, 22, 23], which is called the mass transfer rate constant, 1/min. After Eq.(4) is neatened, Eq. (5) can be obtained.

$$\ln \frac{C^*}{C^* - C_t} = k t + \ln \frac{\pi^2 C^*}{6\left(C^* - C_0\right)} \tag{5}$$

According to equation (5), if the extraction process conforms to the first-order kinetics model, then the relationship $\ln \dfrac{C^*}{C^* - C_t}$ with respect to t is linear. The slope of the straight line is the mass transfer rate constant k, and then C_0 and C^* can be calculated through the intercept of the straight line. Finally, the extraction kinetics equation under each condition can be obtained.

Apparent activation energy

The relationship between mass transfer rate constant k and extraction temperature T conforms to the Arrhenius equation, as shown in Eq. (6) [18, 22, 23].

$$k = k_0 e^{-E_a/(RT)} \tag{6}$$

Where k is the mass transfer rate constant, 1/min; k_0 is the pre-exponential factor, 1/min; R is the gas constant, 8.314 J/(mol·K); T is the extraction temperature, K; E_a is the apparent activation energy, J/mol. The linearization of this expression is shown in Eq. (7):

$$\ln k = \ln k_0 - \frac{E_a}{RT} \tag{7}$$

The values of ln$k$ and 1/T are plotted and fitted linearly. The apparent activation energy of E_a can be obtained from the slope of the straight line.

Half-life period

The extraction time required when the mass concentration of the material drops to half of its original mass concentration is called half-life ($t_{1/2}$), namely, when $t=t_{1/2}$, $C_t=C^*/2$ approximatively [18, 19]. By substituting them into Eq. (5), the Eq. (8) for calculating half-life can be sorted out.

$$t_{1/2} = \ln\left(\frac{8}{\pi} \times \frac{\left(C^* - C_0\right)}{C^*}\right) / k \tag{8}$$

The values of k, C_0, and C^* obtained at each extraction temperature are substituted into Eq. (8) to obtain the half-life

at each extraction temperature. The relationship between $t_{1/2}$ and T can be obtained by graphing the values of $t_{1/2}$ and T and fitting them.

Internal diffusion coefficient

The internal diffusion coefficient D_s characterizes the diffusion capacity of substance molecules in the solid phase, and its value will directly affect the mass transfer rate. According to the above definition $k\left(\pi^2 D_s / r^2\right)$ [18, 22, 23], the D_s value can be calculated from the obtained k value and the known r-value of the mass transfer distance.

Relative raffinate rate

The relative raffinate rate Y_e refers to the proportion of the amount of solute remaining in the material after extraction, which is expressed by the ratio of the mass concentration. The expression of Y_e can be approximately written as Eq. (9) [22, 23]:

$$Y_e = \frac{C^* - C_t}{C^*} \tag{9}$$

The Y_e value at each extraction temperature is calculated by using the experimental data, and the relationship between Y_e and t is fitted by making $Y_e \sim t$ diagram.

Thermodynamics analysis

When the extraction operation reaches a dynamics balance, the relationship between the equilibrium constant K of the extraction process, the thermodynamic parameters of the Gibbs free energy ΔG, the enthalpy change ΔH and the entropy change ΔS and extraction temperature T can be expressed by Van 't Hoff equation, as following Eq. (10) [16, 17].

$$\ln K = \ln\left(\frac{C^*}{C_\infty - C^*}\right) = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

Where K is the equilibrium constant in the extraction process; C_∞ is the maximum mass concentration extracted, mg/mL; ΔG is the Gibbs free energy, kJ/mol; ΔH is the enthalpy change, kJ/mol; ΔS is the entropy change, J/(mol·K); C^*, R and T as above.

The values of K, ΔG, ΔH, and ΔS of the foxtail millet polysaccharides extraction process can be calculated by Eq. (10).
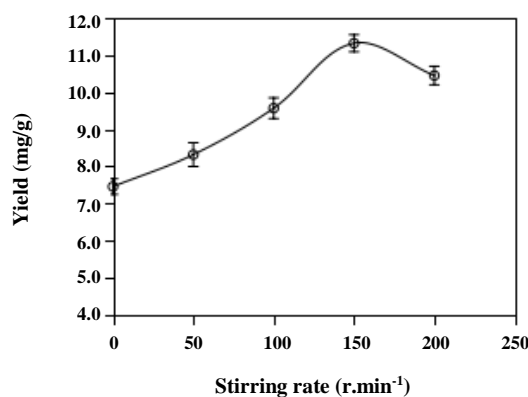

Fig. 1: Effect of stirring rate on yield.

RESULTS AND DISCUSSION
Extraction experiment
Preliminary experiment

In order to select suitable conditions, the effects of stirring rate and liquid material ratio on polysaccharides yield were investigated before the dynamics experiment.

Effect of stirring rate on yield with the whole particle of foxtail millet the effect of stirring rate on polysaccharides yield was investigated under liquid material ratio 20 mL/g, extraction temperature 70.0 ℃, and extraction time 2.0 h, as represented in Fig. 1.

Fig. 1 showed that the polysaccharides yield first increased with the increase in stirring rate, and then the yield decreased after 150 r/min. The reason is that the agitation accelerates the transfer and diffusion of materials in the fluid for diffusion-controlled systems [24]. However, after the stirring rate reached a certain value, the stirring rate increased continuously to cause the increased extraction rate. The time required for polysaccharides extraction was shortened and polysaccharides were basically completely extracted from the material. On the contrary, the polysaccharides extracted into solvent were subject to thermal decomposition for a longer time, so the yield was reduced. The results were the same as that in the study of *Zhu, et al.* (2013) [25]. Therefore, the appropriate stirring rate for polysaccharides extraction was determined to be 150 r/min.

Effect of liquid material ratio on yield

At extraction temperature 70 ℃, stirring rate 150 r/min, and extraction time 2.0 h, the effect of liquid material ratio on the yield of polysaccharides was studied using the whole particle of foxtail millet. The results were shown in Fig. 2.
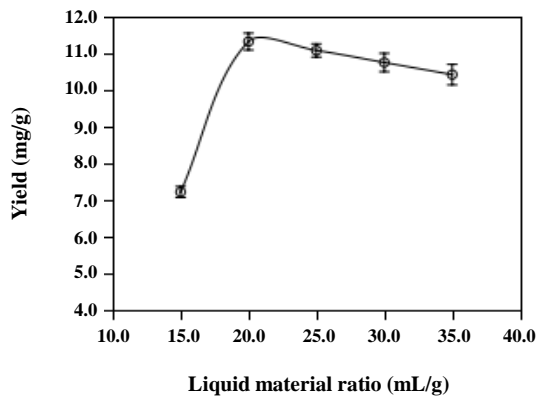
Fig. 2: Effect of liquid material ratio on yield.

Fig. 3: Relationship of C_t and t at different temperatures.

As seen in Fig. 2, the polysaccharides yield first increased with the increase of the liquid material ratio. This was because the mass concentration of polysaccharides in solution was diluted and decreased with the increase of liquid material ratio, which increased the mass concentration difference of polysaccharides between the solid phase and liquid phase and increased the mass transfer force in the mass transfer process. At the same time, the dilution also reduced the viscosity of the solution and the mass transfer resistance [26]. Thus, the transfer rate was accelerated and the number of polysaccharides extracted was increased at the same time. The yield of polysaccharides was the highest when the ratio of liquid to the material was 20.0 mL/g, and then the yield decreased. This reason may be the increase of degradation and loss caused by the prolonged time of subsequent operation (filtration, concentration, alcohol precipitation, etc.) because of the increase in liquid volume. The results were similar to those found by *Xu et al.* (2014) [26] and *Shang, et al.* (2019) [27]. The increase in the liquid material ratio will bring about a series of effects, such as the increase in the amount of extraction solvent, the increase in the time of subsequent separation operation and energy consumption, etc. Therefore, the appropriate liquid material ratio was 20.0 mL/g at extracting polysaccharides.

As a result, the whole particle of foxtail millet, 150 r/min stirring rates, and liquid material ratio of 20.0 mL/g was adopted in the kinetics extraction experiments for observing the influence of extraction temperature and extraction time on the extraction effect.
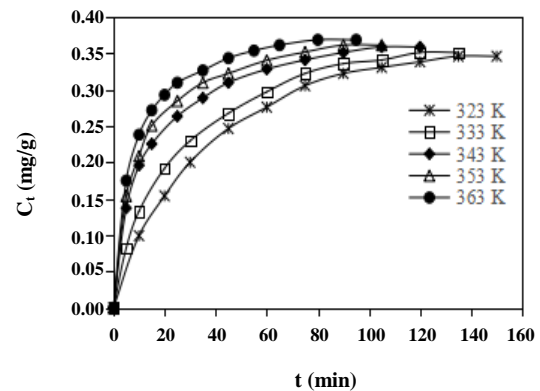
Kinetics extraction experiments

Kinetics extraction experiments were carried out using the whole particle of foxtail millet under the conditions of 323, 333, 343, 353, and 363 K at the liquid material ratio of 20.0 mL/g and the stirring rate of 150 r/min. The changes in polysaccharides mass concentration in the extraction solution with extraction time were determined at different extraction temperatures. The results were shown in Fig. 3.

It is evident from Fig. 3 that polysaccharides concentration increased rapidly with increasing time during the initial phase, followed by slowly increasing and near-saturation during later stages of extraction; the higher the extraction temperature, the higher the mass concentration obtained in the same extraction time, the shorter the time required for the mass concentration in the extraction solution to reach the highest value and the higher the maximum mass concentration that can be reached. This variation tendency of concentration with temperature and time is consistent with that reported by *Krishnan et al.* (2016) [16], *Guo et al.* (2018) [22], and *Najdanovic-Visak, et al.* (2017) [28]. This is because, with the increase in extraction temperature, the cell wall breaking time is shortened, the material's molecular permeability is enhanced, and the diffusion coefficient is increased, so the polysaccharides can be more quickly extracted from the material. At the same time, the solubility of polysaccharides in the solution increases, and the solution viscosity decreases, which reduces the mass transfer resistance, and thus the mass transfer rate is accelerated leading to expediting the extraction of polysaccharides and increasing the extraction amount

Table 1: The fitting equation of ln[C* /(C* ─Cₜ)] ~ t and parameters obtained at different temperatures.

T /K	equation	R^2	k /(1/min)	C* /(mg/mL)	C₀ /(mg/mL)
323	$\ln[C^*/(C^*-C_t)] = 0.030\ 9t + 0.084\ 2$	0.991 8	0.030 9	0.345 9	-0.272 4
333	$\ln[C^*/(C^*-C_t)] = 0.032\ 5t + 0.084\ 4$	0.994 1	0.032 5	0.351 0	-0.179 1
343	$\ln[C^*/(C^*-C_t)] = 0.036\ 8t + 0.362\ 7$	0.992 5	0.036 8	0.358 7	-0.051 4
353	$\ln[C^*/(C^*-C_t)] = 0.041\ 5t + 0.450\ 4$	0.993 3	0.041 5	0.361 2	-0.017 1
363	$\ln[C^*/(C^*-C_t)] = 0.050\ 9t + 0.493\ 2$	0.992 1	0.050 9	0.368 5	-0.001 3
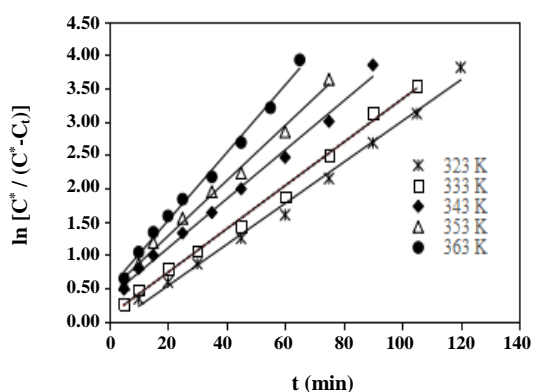
Fig. 4: Relationship of ln[C*/(C*-Cₜ)] and t at different temperatures.

of polysaccharides. In the initial phase, the concentration of solute in the solution increases rapidly due to the large concentration difference, namely, the large mass transfer impetus, the fast mass transfer rate. In the later stage, the concentration difference decreases, reducing the mass transfer rate, so the solute concentration in a solution tends to increase slowly until it reaches saturation. [16, 22, 28].

Kinetics research
Model fitting

The experimental data of polysaccharides mass concentration under different extraction times at different extraction temperatures obtained above were fitted with the first-order kinetics model. That is to say that the data were converted to $\ln[C^*/(C^*-C_t)]$, and the values of $\ln[C^*/(C^*-C_t)]$ and extraction time t were plotted. The results were shown in Fig. 4. The linear equation obtained by fitting and the parameters obtained by calculation were shown in Table 1.

It can be seen from Fig. 4 and Table 1 that the linear relationship obtained by fitting the experimental data at each extraction temperature is good. Each linear regression coefficient R^2 is greater than 0.99. It shows that the extraction process of foxtail millet polysaccharides can be described by the first-order kinetics model. At the same time, the data in Table 1 shows that the value of the straight-line slope k gradually increases with the increase of the extraction temperature, indicating that the increase of the extraction temperature is conducive to the extraction of polysaccharides, namely, the extraction rate of polysaccharides increases. The main reasons are increasing molecular diffusion coefficient and decreasing liquid viscosity [16]. In the current aqueous extraction study, the time versus concentration plots well fit with the first-order model ($R^2 > 0.99$) in the same manner as reported previously for sage (*Salvia fruticosa* Miller) leaves [18], grape marc [19], Chinese prickly ash [22], for *Tussilago faifare* [23].

Apparent activation energy

According to equation (6), the natural logarithm of k values in Table 1 was calculated, and a graph between ln$k$ versus 1/T was plotted. Graphically in Fig. 5.

Fig. 5 showed that the linear regression coefficient R^2 of the experimental data was 0.942 1, indicating that the linear relationship between ln$k$ and 1/T was good. The apparent activation energy E_a of 12.03 kJ/mol in the extraction process of foxtail millet polysaccharides under the experimental conditions was calculated according to the straight-line slope fitted in Fig. 5. The value of E_a was close to 10.47 kJ/mol for hot water extraction of polysaccharide from *Tussilago farfara* [23]. The apparent activation energy value was positive, indicating that the extraction process was endothermic [16]. The result is
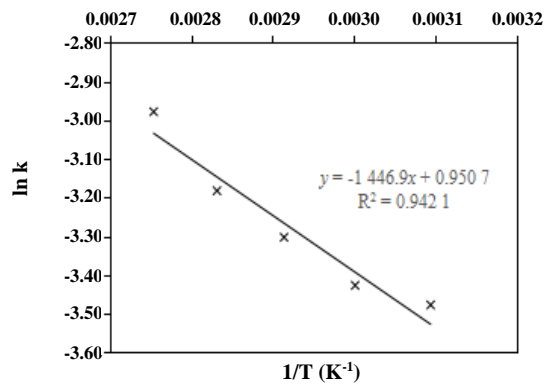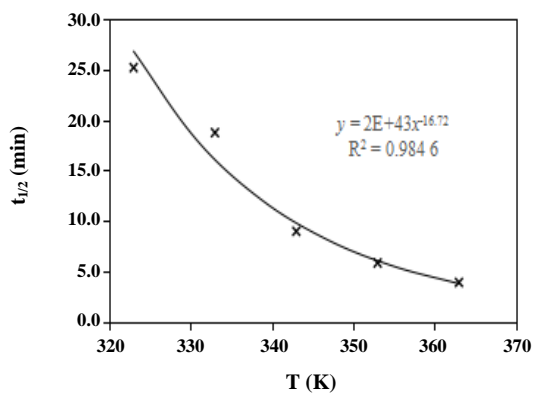
Fig. 5: Relationship of lnk and 1/T.

Fig. 6: Relationship of $t_{1/2}$ and T.

in agreement with the findings of previous studies on different materials [16, 18, 19, 22, 23, 26, 28]. Therefore, increasing the extraction temperature can accelerate the extraction rate of polysaccharides from foxtail millet. The expression of the Arrhenius equation was obtained by related as following $k = 2.59 \exp\left(-\dfrac{1446.9}{T}\right)$.

Half-life period

The values of k, C_0, and C^* at each extraction temperature in Table 1 were substituted into Eq. (7) to calculate the half-life $t_{1/2}$, and the results were shown in Fig. 6.

Fig. 6 showed that the half-life $t_{1/2}$ and the extraction temperature T can be fitted to a power function. The relational expression between $t_{1/2}$ and T was $t_{1/2} = 2 \times 10^{43} T^{-16.72}$. The regression coefficient R^2 of the relationship was greater than 0.98, indicating that

the correlation was good. It can be seen from the curve trend in Fig. 6 that the half-life decreased with the increase of the extraction temperature. The half-life decreased from 25.2 min to 3.9 min with the increase of the extraction temperature from 323 K to 363 K. The reason is that the extraction rate of polysaccharides is accelerated due to the increase in extraction temperature. The shortening of half-life is beneficial to reduce the volume of equipment or improve the production capacity of equipment, which can improve efficiency. This variation tendency is in agreement with that reported in reference *Torun et al.* (2015) [18] and *Sant'Anna et al.* (2013) [19]. The $t_{1/2}$ values decrease with increasing temperatures, indicating augmentation in the rate of extraction at higher temperatures.

Internal diffusion coefficient

Dry foxtail millet particles are about 0.001 m in diameter. Since the mass transfer distance is the radius, r is 0.0005 m. The corresponding internal diffusion coefficient D_s can be obtained by using the k value at each extraction temperature in Table 1 according to its definition formula, and a $D_s{\sim}T$ diagram was made. The results were shown in Fig. 7.

The D_s value increased from 7.84×10^{-10} m^2/min to 1.29×10^{-9} m^2/min as the extraction temperature increased from 323 K to 363 K. The D_s values were similar to those reported in reference by *Torun et al.* (2015) [18]. This is due to the higher the extraction temperature, the smaller the viscosity of the solution, the stronger the molecular thermal movement, and the faster the molecular diffusion. Similar results were published by extracting soluble solids, phenolics, and flavonoids from sage (*Salvia fruticosa* Miller) leaves by *Torun et al.* (2015) [18] and for oils from spent coffee grounds by *Najdanovic-Visak et al.* (2017) [28]. Fig. 7 showed that the experimental points can be fitted into a quadratic equation with one variable. The regression coefficient R^2 was greater than 0.99. The relational expression between D_s and T can be expressed as $D_s = 0.0003T^2 - 0.1864T + 30.75$.

Relative raffinate rate

According to the experimental data, the relative raffinate rate Y_e at each extraction temperature was calculated according to Eq. (9) and the diagram of $Y_e{\sim}t$ was drawn. The results were shown in Fig. 8.
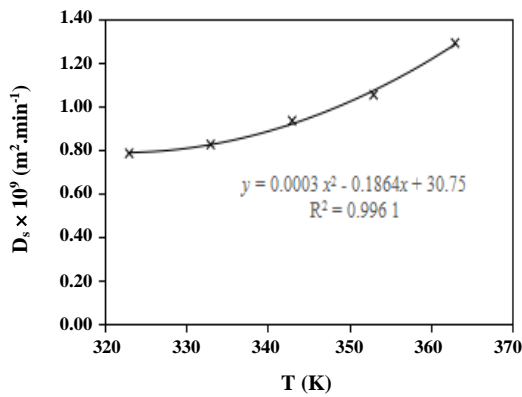
Fig. 7: Relationship of D_s and T.

Fig. 8: Relationship of Y_e and t at different temperatures.

Fig. 8 showed that the relative raffinate rate decreased with the increase of extraction temperature or the extension of extraction time. The decreasing amplitude of Y_e with extraction time at the same extraction temperature was first faster and then slower. It indicates that in the early stage of extraction, especially in the first 10 min, the solute will be removed in large quantities from the material. But the extraction rate slowed down in the later period. Therefore, comprehensive consideration of extraction effect, equipment size, capacity, etc., is not the longer the better extraction time [22]. Fig. 8 showed also that the relationship between Y_e and t at each extraction temperature presents an exponential relationship; each expression was shown in Fig. 8. The R^2 value of each expression was greater than 0.99. *Guo et al.* (2018) [22] and *Zhao and Zhang* (2012) [23] also observed similar behavior during the extraction of polyphenols from Chinese prickly ash and polysaccharide from *Tussilago faifare*, respectively.

Thermodynamics analysis

Polysaccharides were extracted under the conditions of the whole particle of foxtail millet, liquid material ratio 20.0 mL/g, and stirring rate 150 r/min. According to Fig. 3, the extraction process of 363 K was basically balanced at 80 min. The polysaccharides equilibrium mass concentration C^* at this moment was taken as the maximum polysaccharides mass concentration C_∞ of the system. That is, the value was approximatively used as the natural mass concentration of polysaccharides in the material under experimental conditions. The chart of $\ln\left[C^*\big/\left(C_\infty - C^*\right)\right] \sim 1/T$ was drawn and the result was shown in Fig. 9.
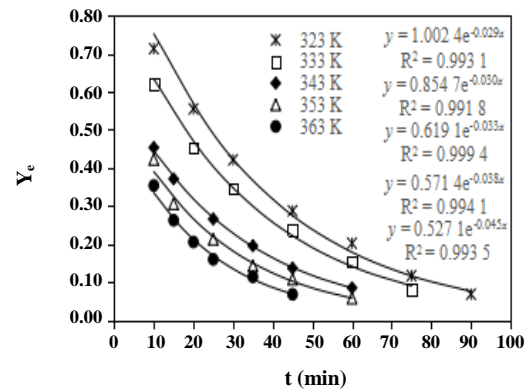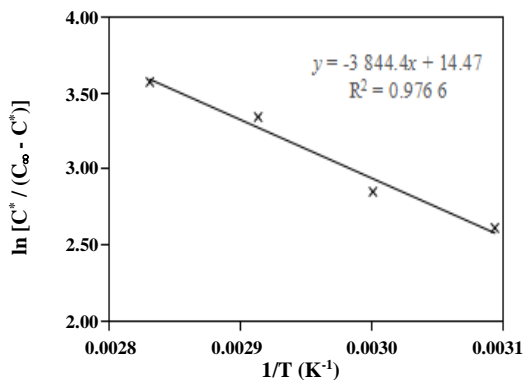
Fig. 9 showed that the relational expression of $\ln\left(\dfrac{C^*}{C_\infty - C^*}\right) = -\dfrac{3844.4}{T} + 14.47$ can be obtained by linear fitting the experimental data. The regression coefficient R^2 was 0.9766, indicating that the linear relationship was fine. The slope and intercept of the straight line are $-\Delta H/R$ and $\Delta S/R$, respectively. Thus the values of thermodynamic parameters of the extraction process of enthalpy change ΔH and entropy change ΔS can be calculated and obtained. The Gibbs free energy ΔG values of the extraction process were calculated according to Eq. (9). The detailed results were summarized in Table 2.

Within the scope of the experimental extraction temperature, the value ΔH and ΔS of *the* extraction process was 31.96 kJ/mol and 120.3 J/(mol·K) respectively, which were all greater than zero. The positive value of enthalpy means that the extraction process of polysaccharides is endothermic; the positive value of entropy indicates the increase in disorder of the solid-liquid extraction system due to the solute transfer from the more ordered solid phase to the less ordered liquid phase, entropy increased of the process makes the process irreversible, and the greater the value, the easier the process is to proceed [16, 17]. The ΔG values of each extraction temperature were all less than zero, which showed that the extraction process can occur spontaneously. The value of ΔG decreased gradually with the increase of extraction temperature, indicating that increasing the extraction temperature can make the extraction process proceed more easily [16, 17].

Table 2: The values of ΔH, ΔS and ΔG at different temperature.

T /K	ΔH /(kJ/mol)	ΔS /(J/(mol·K))	ΔG /(kJ/mol)
323			-6.90
333	31.96	120.3	-8.10
343			-9.30
353			-10.51

$y = -3\,844.4x + 14.47$
$R^2 = 0.976\,6$

Fig. 9: Relation of ln[C*/(C∞-C*)] and 1/T

CONCLUSIONS

The extraction of polysaccharides from the whole particle of foxtail millet by hot water was studied. The results showed that stirring rate and liquid material ratio had an obvious effect on the yield of polysaccharides, the equilibrium mass concentration of polysaccharides in the extraction solution increased and the extraction time needed to reach the equilibrium was shortened with the increase of extraction temperature under the study conditions. The first-order kinetics extraction model can better be used to describe the extraction process of polysaccharides from foxtail millet. The apparent activation energy of the polysaccharides extraction process was 12.03 kJ/mol. The half-life decreased and the internal diffusion coefficient increased with the increase in extraction temperature. The thermodynamic parameters revealed the extraction process of foxtail millet polysaccharides to be endothermic, spontaneous, and irreversible. The research results obtained can provide a reference for the design and optimization of extraction process conditions, equipment design, and process control of foxtail millet polysaccharides.

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