Kinetic dependences for the extraction of apricot pits kernels with ethanol-water solvent

Karim Gafurov, Bobirjon Muslimov, Uktam Saidmuratov, Fируза Kuldosheva, Ravshan Ibragimov and Umid Rakhmatov
Bukhara Engineering Technological Institute, Bukhara, Uzbekistan

E-mail: kgafurov@yahoo.com

Abstract. During the extraction of a capillary-porous body, such as the nuclei of fruit seeds, the movement of the distributed substance in the solid phase is carried out by means of molecular diffusion. The amount of material flow in a solid per unit surface is determined by Fick's law using the diffusion coefficient. The molecular diffusion coefficient depends on the structure of the solid, temperature and soluble substances, and does not depend on the hydrodynamic conditions on the surface of solid particles and the design of the apparatus. The article studies the kinetics of extraction of petals of apricot kernels with ethanol-water solvent. When calculating the value of the residual mass content of plant raw materials during the extraction process, an interval calculation method was used. Based on the experimental data of the extraction kinetics, the molecular diffusion coefficient was determined, which significantly increases during 600-700 s of extraction, and then decreases by 2 times after 1800 s. After 3000 s from the beginning of the process, the diffusion coefficient decreases less sharply. A significant increase in the diffusion coefficient at the beginning of the extraction process, including the impregnation stage, is associated with the uneven distribution of the extracted components in the initial sections of the capillaries. In the studies carried out, the nature of the change in the diffusion coefficient over time does not contradict modern concepts of the mechanism of extraction of a porous structure from plant raw materials.

1. Introduction

The theoretical laws of the extraction kinetics are presented in [1,2]. Extraction as a process for capillary-porous bodies includes 4 main stages:

- the penetration of the extractant into the pores of the capillary-porous body;
- dissolution of target elements;
- internal diffusion, i.e. transfer of matter from the depth of a particle of a capillary-porous body to the interface;
- external diffusion, i.e. transfer of the extractable substance from the interface into the interior of the solvent.

The driving force of the process is the difference in the concentration of the target component in the liquid filling the pores of the solid and in the bulk of the extractant in contact with the surface of the solid particles.

According to Fick's first law [1], diffusion in the phases participating in mass transfer occurs because
of random thermal motion of molecules, atoms, ions, colloidal particles, leading to the transfer of matter from a zone of high concentrations to a zone of low ones:

$$\frac{dM}{dSd\tau} = -D \frac{dC}{dn}$$

(1)

where $dM$ is the mass of the diffused substance; $dS$ - elementary surface normal to the direction of diffusion; $d\tau$ - time; $D$ is the diffusion coefficient; $dC/dn$ - concentration gradient.

In a stationary medium, the differential equation of molecular diffusion, which is called Fick's second law, looks like this [2,3]:

$$\frac{\partial C}{\partial \tau} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

(2)

Where $\tau$ is the time, $x$ is the coordinate; $C$ is the concentration of the diffusing substance.

The concentration field, which describes the distribution of extractives in the volume of a particle, is calculated using the equation [3]:

$$\frac{\partial C}{\partial \tau} = D \left( \frac{\partial^2 C}{\partial \xi^2} + \Gamma \frac{\partial C}{\partial \xi} \right)$$

(3)

where $\xi$ is the generalized coordinate (for the plate $\xi = x$); $\Gamma$ is a constant value depending on the shape of the particles (for plate 0).

The initial condition (concentration inside the body at the initial moment of time) for equation (2):

$$C(x, y, z, 0) = C_0$$

(4)

where $C_0$ is the initial concentration, kg/m^3.

Since we are considering diffusion mass transfer, the boundary conditions of the third kind according to [3] have the form:

$$-D_M \left( \frac{\partial C}{\partial n} \right)_n = \alpha (C_n - C_1)$$

(5)

where $C_1$ is the concentration of the solute in the external environment, kg/m^3; $D_M$ is the coefficient of mass conductivity; $\alpha$ - coefficient of mass transfer, kg/m^3.

Using equation (3) under boundary conditions (4) and (5), it is possible to determine the distribution of concentrations over the volume of the body in time [1].

2. Materials and methods

As an extractant, rectified ethyl alcohol of the "Extra" brand (State standard Р 51652-2000) and tap water specially prepared in accordance with the standards specified in the pharmacopoeia monograph PhS 42-2619-89 were used.

To obtain the required concentration (strength) of the "ethanol + water" solution, you can use the formula:

$$X = \frac{100N-P}{M} - 100P$$

(6)

Where $N$ is the initial concentration of alcohol, %; $M$ is the initial concentration of the solution,%; $P$ is the coefficient, $P=V/100$, $V$ is the volume of the initial solution, ml; $X$ is the amount of water to be added to the original solution, ml

Apricot kernels of the Subkhani variety, harvest 2019, were used as raw materials. The seed kernels were washed with running water and dried in a cabinet dryer at a temperature of 50 °C to a moisture content of 7-8%. Then the seeds were crushed to a predetermined size. Apricot kernels were flattened on rolls in the form of petals.

To determine the average particle size in the form of a plate, the thickness of the petals was measured with a micrometer and calculated by the formula:
\[ \delta_{av} = \frac{100}{\Sigma \frac{\delta_i}{N_i}} \]  

(7)

Where \( \delta_{av} \) is the average plate thickness, mm; \( \delta_i \) is the particle size, mm.

The resulting petals had a thickness of \( \delta=0.3-0.35 \) mm.

A sample weighing 200 g was prepared from the petals. After that, the sample was placed in the container of the extractor. At specified time intervals, samples of the extract were taken for analysis. The temperature in the extractor was 50 °C.

Soluble substances extracted from plant raw materials are a mixture of biologically active compounds of complex chemical composition, therefore, the quantity of extractive substances will serve as a qualitative indicator of each of the extracts.

The technique based on the interval calculation method is widely used in calculating the value of the residual mass content of plant materials during the extraction process [1,5,6,7]. In this case, the extraction curves are divided into intervals, and samples of the extract and the remainder of the raw material are taken at such intervals so that they can serve as time intervals when determining the current concentration.

The concentration of the liquid phase is determined by the refractometric method on a digital refractometer DR301-95 by A.KRÜSS Optronic GmbH, and the decrease in the mass content of the solid phase is determined by the method [8].

In this case, the residual content of extractives in absolutely dry plant material in percent (\( X \)) is calculated by the formula:

\[ X = \frac{m \cdot 100 \cdot 100 \cdot V}{a \cdot (100 - W) \cdot 25} \]  

(8)

Where \( m \) is the mass of dry residue, g; \( a \) - weighed amount of medicinal plant raw materials, g; \( V \) is the volume of the extractant used in a single processing of medicinal plant materials in determining the mass content, ml; \( W \) is the moisture content of plant materials, %.

The design and principle of operation of the laboratory facility are given in.

3. Results and discussion

As it is known [1,2], the molecular diffusion coefficient depends on the structure of the colloidal-porous body, temperature and type of soluble substances don’t depend on the design of equipment and hydrodynamic conditions on the surface of solid particles.

The pore structure is largely determined by the extraction mechanism of the extracts and the rate of its flow. The particle size of the kernels of apricot kernels is much larger than the pore diameters, so they can be taken as isotropic porous bodies.

The current concentration of extractives in the solid phase (g / g, with subsequent conversion in% dry matter) was found using the material balance equation [3,4]:

\[ M_m \cdot (C_0 - \bar{C}) = M_l \cdot C_1 \]  

(9)

Where \( M_m, M_l \) is the mass of dry raw materials and extractant, g; \( C_0 \) - initial concentration of extractives in the solid phase, g/g; \( \bar{C} \) current concentration of extractive substances in the solid phase, g/g; \( C_1 \) - the current concentration of extractives in the liquid phase, g/g.

In [3,4], through the theoretical solution of the molecular diffusion equation, an expression was obtained to determine the value of the diffusion coefficient for the shape of an unbounded plate, which is suitable for any solvent:

\[ D = \frac{9.21R^2}{\pi^2\tau} \left( \frac{8}{\pi^2} - \frac{\bar{C} - C_1}{\bar{C} - C_0} \right) \]  

(10)

Where \( R \) is a certain size (for a plate - half of its thickness); \( \bar{C} \) is the average value of the concentration of the diffusing substance, kg/m³.
The results of experiments on the kinetics of extraction are shown in figure 1, and the results of calculations of the diffusion coefficient calculated by formula (10) are shown in figure 2.

As can be seen from figure 1, the intensive extraction of extractives from raw materials proceeded for 1200 s from the open pores and capillaries of the petals of the kernels of apricot kernels.

Further, the process of transition of extractives to the solvent proceeded more slowly and after 3600 s the equilibrium state of the process practically came. Thus, after the indicated time, further extraction was technologically impractical.

![Figure 1. Dependence of the extraction of extractives from the petals of apricot kernels on time.](image1)

![Figure 2. Dependence of the diffusion coefficient on the extraction time.](image2)

It can be seen from the graph (figure 2) that the diffusion coefficient increases significantly within 600-700 s, and then decreases by half after 1200 s of extraction. After 3000 s from the beginning of the process, the diffusion coefficient decreases less sharply. This can be explained as follows: a significant increase in the diffusion coefficient at the beginning of the extraction process, including the impregnation stage, is associated with the uneven distribution of the extracted components in the initial sections of the capillaries, a further decrease in the diffusion coefficient value is associated with the difficulty of the dissolution processes and the transition of components from the depth of the particle of the capillary-porous body to the interface.
4. Conclusion
In the studies carried out, the nature of the change in the diffusion coefficient over time does not contradict modern ideas about the mechanism of extraction of a capillary-porous structure from plant raw materials, which include the kernels of fruit seeds.

The established parameters of the kinetic dependences and the diffusion coefficient can be used in technological calculations of the process of extraction of apricot kernels with an ethanol-water solvent.

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