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DEVELOPMENT OF ENVIRONMENTALLY SAFE TECHNOLOGIES FOR THE EXTRACTION OF PLANT RAW MATERIALS

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Abstract. The peculiarity of solid bodies of organic origin, in contrast to solid bodies of mineral origin, is that their internal structure is characterized by the presence of two spaces – cellular and intercellular. Such bodies tend to swell upon contact with the extractant. The phenomenon of swelling, during extraction, is always accompanied by the dissolution of target substances contained in the cellular and intercellular space. All these processes create conditions for the diffusion of the dissolved target substance through the cell membrane into the intercellular space, and then through the intercellular space beyond the boundaries of the solid phase particle. This helps to increase the volumes of the cellular and intercellular environment. The absolute value of the volumes of cellular and intercellular spaces is one of the most important values when developing and calculating extraction processes and forecasting environmentally safe technologies for obtaining biologically active compounds. The work presents a method of experimentally calculating the volumes of intercellular and cellular spaces of medicinal plant raw materials of various morphological organs. The established absolute values of the volumes of the cellular and intercellular spaces make it possible to calculate the order of diffusion coefficients of biologically active compounds in the medium of the intercellular space, as well as in the cell membrane. In the future, the determined values of the volumes provide grounds for predicting the regime, kinetics and dynamics of extraction of target substances during the implementation of an environmentally safe technology for obtaining biologically active compounds in production, as well as to support the monitoring of production processes of extraction in digital mode.

Keywords: swelling, cellular and intercellular space, extraction, biologically active compounds.

1. Introduction

Obtaining biologically active compounds (BAS) by the method of extraction from plant raw materials does not lose its relevance over time. Such compounds are still used in the food, pharmaceutical, chemical and other industries in Ukraine and abroad. This applies primarily to countries such as China and India, where plant raw materials are traditionally used as a source of biologically active compounds, as well as countries with well-developed chemistry of organic synthesis, in particular the USA, Japan, Germany, etc. Growing requirements for the qualities of compounds obtained by the extraction method determine the need for the development of more modern technologies for their production and methods of analytical calculation of the main kinetic constants with the use of digital technologies (Kalyuzhny, 2000).

An important argument in favour of obtaining (BAS) by the extraction method is the fact that desalinated water or alcohol solvents are most often used as extractants, which are considered environmentally safe, which makes such productions generally not harmful to the environment, but is of great importance in the modern civilized world of

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production and exploitation of chemicals (Akselrud, Lisjansky V, 1974; Harna, 2012).

Extraction processes from plant raw materials are traditionally time-consuming. The reason for this is the anatomical structure of plant raw materials, since the main component of such solid bodies is the cell, the internal volume of which is limited by the cell membrane. To conduct experimental studies, we chose the roots of Altea medicinal and Plantain leaves. Due to the physical characteristics of a cell membrane, it is the main resistance to the diffusion of ALS into the intercellular space. Today, many factors are known that can intensify the process of diffusion through the cell membrane, but most of them lead to the loss of the optical activity of a complex molecule of organic origin and sometimes to the loss of the biological activity of the target compound. This is an unacceptable factor in the chemical and pharmaceutical industry because a therapeutic dose does not provide a therapeutic effect. In food technology, all the principles of nutrition science are violated. In chemical technologies, the quality of products obtained from such raw materials cannot withstand criticism (Dyachok et al., 2015).

Mathematical descriptions of extraction from solid bodies of the cellular structure, including vegetable raw materials, can be found in the literature (Kotov, Bandura, 2018; Dyachok et al., 2017; Dyachok, Zaporozhets, 2017; Dahmoune et al., 2015; Dyachok et al., 2021). To use them efficiently, the volumes of cellular and intercellular space should be known. Actually, in this work, a successful attempt was made to determine these quantities experimentally.

The purpose of the work is the theoretical justification and practical development of the prerequisites for establishing the absolute values of the volumes of the cellular and intercellular spaces by the swelling method.

2. Experimental part

The most common theory of mass transfer processes of extraction in the solid-liquid system assumes that the target substance within the volume of the solid can be in a solid or liquid aggregate state. The extractant penetrates the pores of the extraction object, dissolves the target substance and creates conditions for diffusion of the latter to the outer surface. Regardless of the aggregate state of the target substance, the skeleton of the solid during extraction remains unchanged and performs the role of an inert carrier. Fick's law, which is the differential equation of molecular diffusion, is used to describe the extraction from such bodies. It proceeds in a non-stationary (undetermined) diffusion mode, that is, when the concentration of the target substance at each point changes. In a one-dimensional linear coordinate system (concentration is a function of only one linear coordinate and time – x, t), and in a Cartesian coordinate system (concentration is a function of three coordinates and time – x, y, z, t). In this case, this equation, under the condition of a constant value of the diffusion coefficient, has the form (Dyachok et al, 2015). During extraction, the kinetics of the process is characterized by mass transfer coefficients, the absolute values of which ultimately determine the mass transfer coefficient as a whole. Determining their values and establishing the conditions for achieving their maximum values plays a fundamental role in all mass transfer processes, including extraction. Traditionally, the driving force of extraction processes is considered to be the concentration difference of the target substances in the phases in which the mass transfer is implemented. Therefore, under conditions of equilibrium, a particular value of the concentration of the target substance in the liquid phase corresponds to a determined concentration of substances in the solid phase and is analytically calculated in both phases using the mass transfer material balance equation. All this applies, as a rule, to solid bodies of mineral or inorganic origin.

A characteristic feature of solid bodies of organic origin is the cellular structure. Such bodies include, as mentioned above, vegetable raw materials. Its internal anatomical structure can be characterized by the presence of two spaces, cellular and intercellular, which are separated by a cell membrane. The structure of cell membranes is quite complex, and, as evidenced by the data of experimental studies, they cause the main resistance to the diffusion of the intracellular target substance into the intercellular space. Therefore, in the most generalized form, the cell is considered a source of the target substance and the intercellular space as a transport corridor.

Both fresh and dry plant material can be subjected to extraction. In the case when we are dealing with dry plant material, the extraction process begins with the fact that the entire space, both intercellular and cellular environment, is filled with the extractant and an opportunity is created for the intracellular substance to diffuse through the cell membrane into the intercellular space, and then to the boundary of the phase distribution. All this complex mechanism of mass transfer is determined by mass transfer coefficients. Establishing and researching a complex of factors that can potentially intensify mass exchange during extraction from solid bodies of cellular origin is important for the extraction process from plant raw materials.

The described complex of diffusion phenomena inside the particles of crushed plant material is currently considered and described by analytical dependencies in the literature (Bartel et al., 2015; Dyachok et al., 2017; Dyachok, Zaporozhets, 2017). At the same time, it is important to skillfully apply the developed theoretical base, and after receiving data from experimental studies of extraction kinetics, calculate the main kinetic coefficients, i.e. determine separately the values of mass transfer coefficients through the cell membrane – k_c and in the intercellular space – km. As experience shows, the values of diffusion coefficients target substances, as well as their order, through the cell membrane - D_c is much smaller than the value of the diffusion coefficient in the intercellular medium – Dm, and the latter, in turn, is much smaller than the molecular diffusion coefficient in the medium of the extractant – D (Dyachok et al., 2018; Dyachok et al., 2015; Dyachok et al., 2017).

In the theoretically derived formula (1) (Kotov, Bandura, 2018):

$$C_1 = C_{1p}\left(1 - \frac{1}{r+1} e^{-Kt}\right), \tag{1}$$

in which $K = k_m - k_c$. (2)

It should be noted that the mass transfer coefficient – K is a value that includes two constants, in particular, the mass transfer coefficient through the cell membrane – k_s and the mass transfer coefficient in the intercellular medium – km. (see equation (2). The mathematical form of equations (1) and (2) provided a careful study of the extraction kinetics, allows determining the values of mass transfer coefficients through the cell membrane – k_c and in the intercellular space – km. Setting the values of the corresponding coefficients in the future according to formulas (3) and (4) allows us to calculate the order of diffusion coefficients through the cell membrane and in the intercellular medium – D_m. The analytical expression for calculating the mass transfer coefficient through the cell membrane can be represented as a dependence:

$$k_c = \frac{D_c}{\delta_c R_{equivalent}}, \tag{3}$$

where $R_{c.equivalent} = \frac{V_c}{F_c}$ is the equivalent cell radius.

k_c is the coefficient of mass transfer through the cell membrane, D_c is the diffusion coefficient through the cell membrane; F_c is the cell surface area; δ is the cell membrane thickness; V_c is the volume of the cellular medium.

The coefficient of mass transfer in the intercellular medium is often called the coefficient of internal mass conductivity and is presented in the form of the following dependence:

$$k_m = \frac{D_m}{dR_{m.ef}}, \tag{4}$$

where $R_{m.ef} = \frac{V_m}{F_m}$ is the effective radius of the extracted particle; D_m is the diffusion coefficient in the intercellular medium; F_m is the surface area of extracted particles; *d* is the diameter of extracted particles; V_m is the volume of the intercellular space.

In most cases for a plant cell, the value *kc* is constant since its cell size and the thickness of its membrane are relatively stable values. The kinetics of extraction of solids of the cellular structure, or more precisely, the total mass transfer coefficient *K*, will be influenced mainly by the value *km*, the absolute value of which will depend on the geometric size of the grinding of the particle *d*, which is to be extracted. So, having studied the kinetics of extraction of solid bodies of cellular structure, which include, as mentioned above, vegetable raw materials of various sizes, from 1 to 5 mm, and having processed the obtained results according to equation (1) in logarithmic coordinates:

$$\ln\left(1 - \frac{C_1}{C_{1p}}\right) = \ln A - K_t, \tag{5}$$

where find the coefficient of mass transfer *K*, for certain sizes of particles of vegetable raw materials. Then we build a graphic dependence *k = f(d)*, based on which we get an analytical dependence, according to which we determine the coefficient of mass transfer through the cell membrane *kc*, then in the intercellular medium *km*.

Thus, based on the developed mathematical theory and known values *kc* and *km*, it becomes possible to determine the order of diffusion coefficients through the cell membrane *Dc*, then in the intercellular environment *Dm*.

The mathematical description obtained based on the theoretical assumptions differ from the traditional solution of the differential equation of non-stationary diffusion in a one-dimensional coordinate system (Dyachok et al., 2015).

$$t \sim R^2. \qquad (6)$$

The results of the extraction kinetics of crushed plant material do not confirm the provision that the time to reach the same concentration value of the target substance in the extractant during extraction from particles of different sizes is proportional to their squared radius (see (6)). Provision (6) works in the case of extraction from solid mineral or inorganic origin.

Taking into account the above, we come to the conclusion that the process of extracting the cellular structure from solid bodies is complex in mechanism and is accompanied by mechanical, and physicochemical phenomena, and it is unacceptable not to take this into account. The developed theory of extraction from solid bodies of the cellular structure will be successfully applied provided that the values of V_c – the internal volume of the cells forming the solid body and V_m – the volume of the intercellular space of the solid body of the cellular structure are known (Kotov, Bandura, 2018; Dyachok et al., 2017; Dyachok, Zaporozhets, 2017; Dahmoune et al., 2015; Dyachok et al., 2021; Hubsky et al, 2007; Lebeda et al, 2010; Pavliuk et al, 2017; Ponomarev, 1976; Savelyeva, Vladimirova, 2015; Yuecheng, Liang, 2014; Riznychenko, 1996).

These two types of plant raw materials are most often subject to extraction for obtaining ALS. They were previously crushed, weighed and loaded into flasks with the same volume of extractant (desalinated water acted as the extractant). Flasks were subjected to mechanical stirring. During the set time intervals, the plant material was successively unloaded from the flasks onto a filter filled with filter paper, and the extract was carefully separated and weighed. Since the water used as an extractant was desalinated, the density of which was conventionally assumed to be 1 g/ml, the value of the absorbed volume of the extractant corresponds to the value of the increase in the weight of the sample. In this way, the volume of the absorbed extractant was determined by the increase in the weight of the sample. The obtained data on the kinetics of solvent absorption by plant material is shown in Fig. 1.

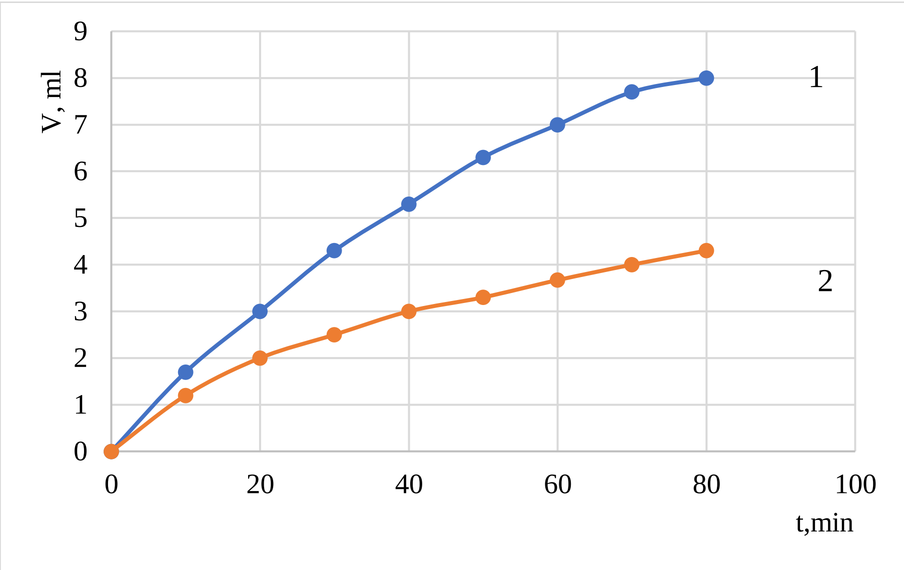

Fig. 1. Kinetics of swelling of the root of *Altea medicinal* -1, *Plantain* leaves -2

3. Results and Discussion

It is important to note that the processes of swelling of plant material are similar to the mechanism of solvent penetration during extraction. So in this case, the water is desalted, then the solvent first enters the intercellular space, and then, through the cell membrane, into the internal volume of the cell. It is also obvious that these processes will be accompanied by a different rate of penetration of the solvent, and therefore a different rate of swelling. It is logical to expect that the rate of penetration of the solvent into the intercellular environment will be much higher compared to the rate of its percolation through the cell membranes into the internal volume of the cell. Accordingly, by plotting the dependence of the swelling speed on the volume of the absorbed solvent, it becomes possible to determine these speeds separately, as well as the volumes of the intercellular and cellular environments, using the graphoanalytical method.

Fig. 2 shows the dependence of the swelling rate of plant material on the volume of absorbed solvent. The obtained results of experimental studies (Fig. 2) indicate that the kinetics of solvent absorption, both of the roots of *Altea* and the *Plantain* leaves, are significantly influenced by the internal anatomical structure of the morphological organs of the plant material. Interpreting the data in Fig. 2, it should be noted that the solvent penetrates into the intercellular medium quite quickly and this period is characterized by a relatively high swelling rate, as can be seen in Figure 2, the curves go sharply upwards. Then, having reached a certain value, they begin to move down. The first obtained maximum on the curves (Fig. 2) indicates that the intercellular medium is sufficiently developed, therefore easily filled with solvent, the swelling rate reaches a certain maximum, which determines the actual volume of the intercellular space.

The area under the first maximum characterizes the volumes of the intercellular medium of roots and leaves, respectively. They are different in absolute size, which is explained by their anatomical structure. For roots, the volume of the intercellular medium is larger, and the filling time is longer compared to leaves.

The further decrease in the swelling rate is explained by the fact that the studied plant material was taken dry. When in contact with soluble, cell membranes are “restored”, then the partial dissolution of some of its target components and, finally, the opening of pores. These phenomena were accompanied by a decrease in the rate of absorption of the solvent, and hence the rate of swelling and, accordingly, the downward movement of curves in Fig. 2.

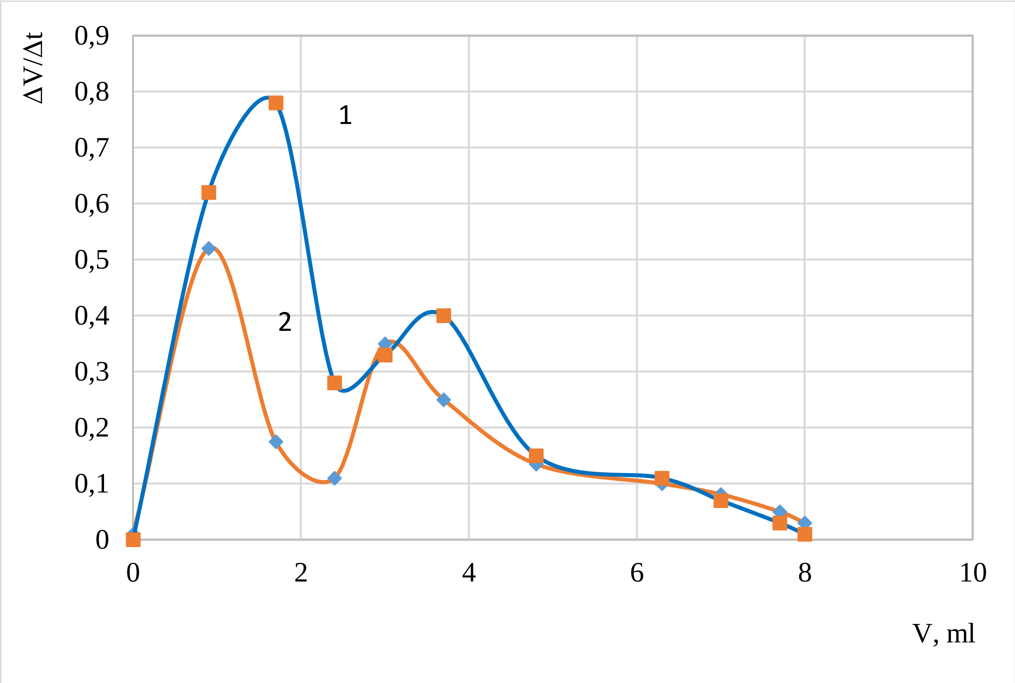

Fig. 2. Regularities of the swelling rate depending on the volume of the absorbed solvent of the roots of *Altea medicinal* –1 and *Plantain* leaves –2

After these phenomena are completed, the solvent quickly penetrates through the pores of the membranes, and at the same time, the process of dissolving the target components in the internal volume of the cells, both of althea roots and plantain leaves, takes place. Therefore, there is a movement of curved tops and an increase in the rate of swelling, which is accompanied by the filling of the volume of the intracellular medium. The area under the curve of the second maximum characterizes the amount of extracted target substances from the internal volume of cells, and the larger it is, the larger the volume of the cellular environment.

In this way, the second maximum is reached, which characterizes the filling of the volume of the cellular environment with the solvent. Subsequently, the diffusion of target substances through cell membranes and beyond the boundaries of the solid phase particles is accompanied by a decrease in the rate of swelling and is depicted by the downward movement of the curve.

The second maximum on the curve (Fig. 2) corresponds to the volume of the cellular medium of the studied plant material. If we subtract the volume of the solvent corresponding to the second maximum from the volume of the solvent corresponding to the first maximum, we get the volume of the cell medium. So, as can be seen from Figure 2, it is possible to experimentally determine the volumes of cellular and intercellular media, as well as to develop theories of optimization of the processes of extraction from solid bodies of the cellular structure (Pavliuk et al, 2017; Ponomarev, 1976; Savelyeva, Vladimirova, 2015; Yuecheng, Liang, 2014).

The developed regularities of the swelling of the roots of *Altea* and *Plantain* leaves are typical for other types of plant material. The obtained result complements the knowledge of the theory of mass exchange processes in the system solid body of cellular structure - liquid, and has a perspective for the development of theories of optimization of extraction processes.

4. Conclusion

A method of determining the absolute values of the volumes of the intercellular and cellular environments of solid bodies of the cellular structure is proposed.

Based on the known values of the volumes of the intercellular and cellular space, it is possible to calculate the values of the diffusion coefficients of biologically active compounds in the intercellular space and through the cell membrane, as well as to establish the mode of the extraction process and predict the dynamics of extraction of target substances during the implementation of technological processes in production conditions.

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