

## MASS TRANSFER IN THE SOLID-LIQUID SYSTEM: MECHANISM AND KINETICS OF THE EXTRACTION PROCESS

*Yevgen Semenyshyn*<sup>1, ✉</sup>, *Volodymyr Atamanyuk*<sup>1</sup>, *Tetiana Rymar*<sup>1</sup>,  
*Oleksandr Ivashchuk*<sup>1</sup>, *Anna Hlukhaniuk*<sup>1</sup>

<https://doi.org/10.23939/chcht14.01.121>

**Abstract.** The mechanism and kinetics of the target components extraction from mineral raw materials (sulfur from sulfur ore by tetrachlorethylene,  $\text{Al}_2\text{O}_3$  from bauxite specs by NaOH, copper from ore and malachite by hydrochloric acid), as well as vegetable oils (from amaranth, amaranth hybrid and camelina by organic solvents) have been studied. Experimental studies to confirm the diffusive nature of the target components extraction from mineral sources have been conducted. Diffusion coefficients for mineral samples have been obtained. It has been established that the target component extraction from the plant raw material occurs by the internal diffusion transfer of the component to the surface of the phase contact and the external diffusion from the surface to the liquid volume. Kinetic and diffusion coefficients for the samples of vegetable raw materials were determined.

**Keywords:** extraction kinetics, solid-liquid system, mineral raw materials, vegetable raw materials, target components.

### 1. Introduction

Mass exchange processes in the solid-liquid system are associated with the extraction of the target components from mineral (uranium, gold, aluminum) and vegetable (oil, target components) raw materials and are widely used in various industries, such as hydrometallurgical, chemical, food, pharmaceutical and others [1-10, 12-19]. A characteristic feature of the target components removal from porous structures by traditional methods is low degree of extraction: 70–72 % in hydrometallurgy, 30–80 % in food industry, 35–50 % in pharmaceutical industry. In some cases, the content of the target component in the porous structure is 0.3–15 %, which

complicates their complete removal by traditional methods [5, 8-10].

A low degree of target components extraction in the existing methods is associated with a large number of different factors that affect this process (the structure of porous material, the particle size of the solid material, the size of pores, temperature, properties of the solvent, the conditions of movement of the target component, process scheme, mechanism of movement). One of the reasons for low oil extraction is imperfection of the technological scheme. Therefore, when extracting vegetable oil in most cases the method of pressing is used. The advantage of this method is simplicity of the technological scheme and the disadvantage is the use of energy-intensive equipment. The main disadvantage of the pressing method is large oil losses (15–20 % with meal) [4].

Thus, these factors contradict the principles of integrated use of raw materials, environmental protection, and efficient operation of technological equipment. Therefore, for complete removal of the target component from the meal, the method of extraction is used, which allows almost 97–98% removal of the target component. Usage of the extraction method is more promising, but it requires development and improvement of technology and further researches. The choice of extraction method for the target component depends primarily on the state of the target component and structure of the porous solid.

Regardless of the state of the target component (solid or liquid), which is in porous structure, the extraction process is considered to occur by complex internal and external diffusion mechanisms. The target component, which is in pores of the solid skeleton, moves to the surface of phase contact due to internal diffusion, and from the surface of phase contact to the bulk of solvent due to external one. These processes occur at different speeds. Internal diffusion transfer of component into the pores of the solid skeleton is the slowest (limiting) step that determines the speed of entire extraction process.

Knowledge of the laws of equilibrium is important to solve the problems involved in establishing the

<sup>1</sup> Lviv Polytechnic National University,  
12, Bandery St., 79013 Lviv, Ukraine  
✉ [yevhen.m.semenyshyn@lpnu.ua](mailto:yevhen.m.semenyshyn@lpnu.ua)

© Semenyshyn Ye., Atamanyuk V., Rymar T., Ivashchuk O.,  
Hlukhaniuk A., 2020

mechanism of extraction process, since the rate of entire process is determined by the magnitude of driving force equal to the difference between equilibrium and working concentration of the solvent. The equilibrium concentration depends on the state of target component in porous structure of the raw material – solid or liquid. For the solid state, equilibrium occurs when concentration of the component in liquid becomes equal to the saturation concentration. In the second case, concentration in the bulk of liquid is equal to concentration in skeletal pores. In some cases, this difference is ignored in calculations.

Thus, the current state of problems associated with application of the extraction method to extract the target components requires solving complex problems that occur in the system “solid-liquid” and are characterized by insufficient knowledge of the kinetic laws of the process, the imperfection of equipment, and the lack of mathematical models. The presence of a mathematical description of these processes can be the basis for designing efficient equipment and for the progress of extraction method for the target components removal.

Since the mentioned method involves internal and external diffusion transfer, this work is devoted to the study of this process mechanism. Determination of kinetic regularities on models will allow to determine experimentally the kinetic coefficients necessary for the calculation of effective mass-exchange equipment for extraction of target components from mineral and vegetable raw materials of different nature.

## 2. Experimental

Studying the mechanism of the extraction process is necessary to determine the slowest stage of the process, as well as kinetic constants. To determine them a mathematical model of kinetics of extraction of solids and liquids has been developed, on the basis of which it is possible to predict the process in real conditions (direct-flow and flow-back processes, joint dissolution and extraction, etc.). For the mathematical model, it was assumed that the particles of solid material had the shape of a sphere with an average diameter  $d_m$ .

Experimental verification of the kinetics of the extraction process from mineral raw materials was carried out at objects related to the extraction of such substances as sulfur from sulfur ore, tetrachlorethylene,  $Al_2O_3$  from bauxite specks by 15 % NaOH solution, copper from ore, and malachite ( $CuCO_3 \cdot Cu(OH)_2$ ) by hydrochloric acid. In addition, plant materials, in particular, rapeseed, amaranth, hybrid amaranth and camelina were used as the studied objects. *N*-hexane and methylene chloride were used as solvents for the extraction of vegetable oils [5, 8-10].

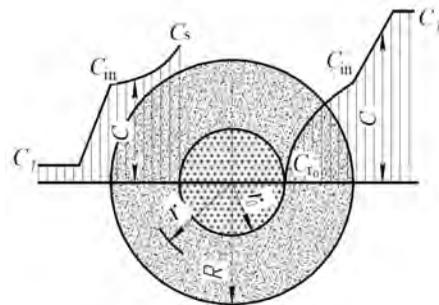
Experimental methods of the extraction process study for mineral raw materials, as well as for grinded and not grinded vegetable seeds, are given in the next section detailing the conditions of the experiment.

## 3. Results and Discussion

To establish the mechanism of the slowest stage of the extraction process and to experimentally determine the diffusion coefficients, we used the equation obtained by the authors in [2, 5]:

$$\tau = \frac{t}{T} = \frac{1 - 3 \cdot \varphi_0^2 + 2 \cdot \varphi_0^3 + \frac{6}{\varepsilon} \cdot (1 - \varphi_0) + \frac{2}{Bi} \cdot (1 - \varphi_0^3)}{1 + \frac{6}{\varepsilon} + \frac{2}{Bi}} \quad (1)$$

where:  $\tau$  is dimensionless time;  $t$  is running extraction time;  $T$  is complete removal time;  $\varphi_0$  is dimensionless radius of the porous particle in which the target component is located;  $\varphi_0 = \frac{r_0}{R}$ , where  $r_0$  is a radius of the sphere in which the target component is located;  $R$  is a particle radius (grain);  $Bi = \frac{K \cdot R}{D}$  is a Bio criterion;  $K$  is a mass transfer coefficient;  $\varepsilon = \frac{K_{r_0} \cdot R}{D}$  is a chemical interaction criterion, where  $K_{r_0}$  is a chemical interaction constant; and  $D$  is a diffusion coefficient.



**Fig. 1.** Scheme of the target component extraction from the porous ball-shaped material [8]

Fig. 1 presents a diagram of the target component extraction from porous material, which has the shape of a ball. The left part of Fig. 1 corresponds to the process of extracting the target component for physical dissolution conditions when it is located in the porous skeleton in a solid state. The right part of Fig. 1 corresponds to the process of extraction under conditions of chemical interaction of reagent with the target component, which is in a solid state.

According to Eq. (1), depending on the conditions of extraction, the following mechanisms take place:

1. Internal diffusion mechanism, for which the slowest stage of process is internal diffusion. This mechanism is characterized by  $\varepsilon = \infty$  and  $Bi = \infty$  and according to Eq. (1) we have:

$$\tau = \frac{t}{T} = 1 - 3\varphi_0^2 + 2\varphi_0^3 \quad (2)$$

2. The mechanism of interphase chemical interaction, for which the slowest stage is chemical interaction. Such mechanism can exist under the condition  $\varepsilon \gg 1$ , then Eq. (1) will have the following form:

$$\tau = \frac{t}{T} = 1 - \varphi_0 \quad (3)$$

Eq. (3) is also valid for the processes of simple dissolution when  $Bi \ll 1$ .

3. The mixed-diffusion mechanism for which the process exists under the condition  $\varepsilon = \infty$ . There is no chemical interaction for this mechanism. However, internal and external diffusion take place, so Eq. (1) has the form:

$$\tau = \frac{t}{T} = \frac{1 - 3 \cdot \varphi_0^2 + 2 \cdot \varphi_0^3 + \frac{2}{Bi} \cdot (1 - \varphi_0^3)}{1 - \frac{2}{Bi}} \quad (4)$$

4. Mixed diffuse-chemical process for which the criteria  $\varepsilon$  and  $Bi$  cannot be neglected.

Among these mechanisms of the extraction processes, there is no external diffusion mechanism, since for the particles in the form of a sphere  $Bi \gg 1$  [2, 5] and the condition  $Bi \ll 1$  is not realized.

We determined the dimensionless radius based on the material balance equation of the extraction process:

$$M_0 \cdot (1 - \varphi_0^3) = W \cdot C_1 \quad (5)$$

where  $M_0$  is a mass of the target component in porous material, kg;  $W$  is a volume of solvent,  $m^3$ ;  $C_1$  is a concentration of the target component in solution at time  $t$ ,  $kg/m^3$ .

Note that the dimensionless radius  $\varphi_0$  varies with the extraction time from  $\varphi_0 = 1$  to  $\varphi_0 = 0$ , which corresponds to the time  $t = 0$  and  $t = T$ , respectively. Therefore, the mechanism of the target component extraction can be established according to the dependency

$\varphi_0 = f\left(\frac{t}{T}\right)$  for different mechanisms according to Eq.

(1) at different values of  $\varepsilon$  and  $Bi$ , and experimentally as well.

Experimental verification of Eq. (1), as well as the determination of the diffusion coefficient were carried out on various objects of industrial value [1-3, 5-10, 11-19]. In Fig. 2 the kinetics of sulfur extraction from tetrachloroethylene ore at different temperatures are presented. Similar studies were performed for  $Al_2O_3$  from bauxite specks with NaOH alkali solution and for copper with hydrochloric acid ore.

According to Eq. (1) for the conditions of internal molecular transfer ( $\varepsilon = \infty$  and  $Bi = \infty$ ), which is the slowest stage of the process, we determined the dimensionless time:

$$\tau = \frac{t}{T} = 1 - 3 \cdot \varphi_0^2 + 2 \cdot \varphi_0^3 \quad (6)$$

According to Eq. (6) there must be a linear dependence between the quantities  $\tau$  and  $t$  (Fig. 3). Such dependence, as shown by experimental studies conducted on many objects of mineral raw materials, does exist [1-3], which indicates a satisfactory alignment of the theory with practice. It should be noted that the kinetic dependences shown in Figs. 2 and 3 reflect the kinetics of processes in which the kinetic curves do not take into account the particles size, but only reflect the similar nature of increase in concentration.

The mechanism of the target component extraction can also be established by comparing the experimental data with the different curves obtained according to Eqs. (2) and (3) (Fig. 4).

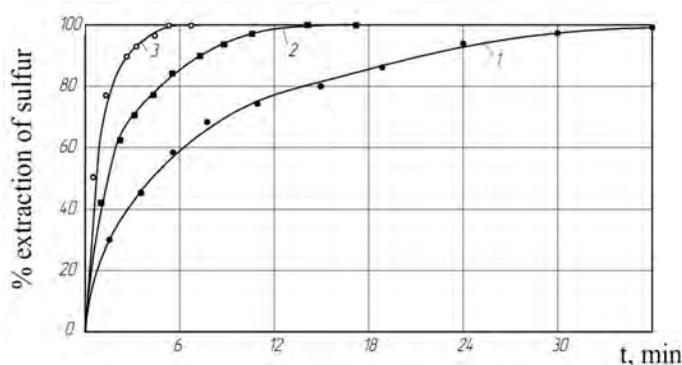
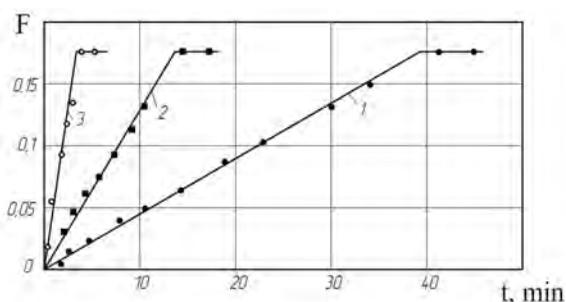


Fig. 2. Kinetics of sulfur extraction from ore by tetrachloroethylene at 353 K (1); 368 K (2) and 383 K (3)



**Fig. 3.** The dependence of the value  $F = \frac{1}{6} \frac{\varphi_0^2}{2} + \frac{\varphi_0^3}{3}$  of the sulfur extraction from ore by tetrachloroethylene on  $t$  at 353 K (1); 368 K (2) and 383 K (3)

We used Eq. (6) to determine experimentally the diffusion coefficient by the slope of the curve  $F = f(t)$  (Fig. 3).

$$D = tg\alpha \cdot \frac{\rho \cdot R^2}{C_s} \quad (7)$$

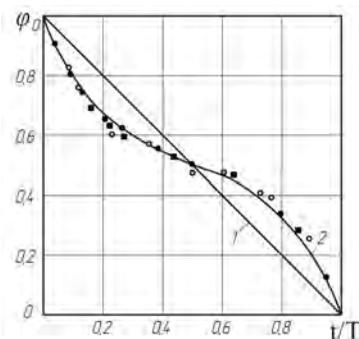
$$tg\alpha = \frac{D \cdot C_s}{\rho \cdot R^2} \quad (8)$$

Experimental verification of Eq. (1) regarding the establishment of the mechanism of target components extraction from porous structures was carried out at the objects of industrial level to extract such target components as  $Al_2O_3$  from bauxite heat, sulfur from sulfur ores, copper from oxidized copper ores, and others.

To determine the mechanism of aluminum oxide extraction, studies were performed in an apparatus with a mixer of appropriate target component mass in the porous material  $M_0$ , with a volume of solvent  $W$  in volume units of 15% NaOH solution. The size of the porous particles differed little from each other and had an average value of  $R = 0.38$  m. The solvent temperature of 323 K was kept constant. At certain intervals, samples were taken from the solution and analyzed for  $Al_2O_3$  content by a trilonometric method, by determining the concentration of  $C_1$ . The value of  $\varphi_0$  was determined from Eq. (5).

Assuming that the process is limited by the internal diffusion of  $Al_2O_3$ , the diffusion coefficient can be determined by the slope according to Eq. (5) at a saturation concentration  $C_s = 0.113$  g/cm<sup>3</sup> and density  $\rho = 3.92$  g/cm<sup>3</sup>. The diffusion coefficient of  $Al_2O_3$  under these conditions is  $D = 1.83 \cdot 10^{-9}$  m<sup>2</sup>/s.

The diffusion coefficients for the extraction of sulfur from the sulfur ore were similarly determined. They were  $1.5 \cdot 10^{-9}$  m<sup>2</sup>/s and  $5.6 \cdot 10^{-9}$  m<sup>2</sup>/s in the temperature range of 373–413 K. The average diameter of the ore particles was  $R = 4$  mm; the sulfur content in the ore was 16.7 % and oil was used as the solvent. Fig. 3 shows that there is indeed a linear relationship between the parameter



**Fig. 4.** Kinetic and diffusion regions of extraction. Curves 1, 2 are constructed according to Eqs. (2) and (3)

$F$  and  $t$ . From Fig. 4, the diffusive nature of sulfur extraction is clearly confirmed.

A similar determination of the diffusion coefficients was experimentally carried out on an artificially created model in which polystyrene was used as a solid porous skeleton and the target component was malachite ( $CuCO_3 \cdot Cu(OH)_2$ ) uniformly located in the inert skeleton. A sulfuric acid solution was used as the solvent. The experiments were performed in an apparatus with a stirrer at the temperatures of 293, 303, 313 and 323 K. The determined diffusion coefficients were  $0.226 \cdot 10^{-9}$ ,  $0.48 \cdot 10^{-9}$ ,  $0.662 \cdot 10^{-9}$  and  $0.974 \cdot 10^{-9}$  m<sup>2</sup>/s, respectively. For comparison, a free diffusion coefficient  $D = 0.38 \cdot 10^{-9}$  m<sup>2</sup>/s was determined at 293 K, which confirms accordance of the experimental values with the theoretical ones.

Significantly more complex is the process of extracting the target components from plant materials. In this case, the process is complicated by the presence of membranes surrounding the cells in which the target component is concentrated. Target components can be in a solid state (stems, leaves, seeds) and in a liquid one (oil) [5-10, 15-19]. In comparison with minerals, a characteristic feature of plant materials, in addition to cellular structure, is the low content of target components (0.3–3 %) and the long duration of the extraction process using infusion method – up to several days.

In some cases, the seed is characterized by the presence of a thin film that protects the grain from the environment. This is characteristic for such seeds as rape, amaranth, soybeans, and others. Therefore, the removal of target components from plant raw materials in comparison with minerals is much more complicated and requires appropriate technology for efficient removal of target components. Taking into account the complexity of the processes involved in extracting the target components from plant materials, its variety of structure and a number of other factors that influence the speed of the target

component extraction, today the methods like infusion, extraction, compression, and a number of others are used. The main methods widely used in the industry include pressing and extraction. Each of these methods has its advantages and disadvantages. The advantage of the press method is relatively simple production technology. The disadvantage is a low degree of removal of target components, a significant energy intensity of technology processes, etc.

In turn, the advantage of the extraction method is the high degree of target components removal, which is 95–98 %, but the disadvantage is the need for expensive solvents, the complexity of individual processes in the technological scheme, etc. [5, 10]. Therefore, effective removal of target components in multi-tonnage production (sunflower oil) is possible in the case of joint use of two methods – pressing and extraction.

Extraction of the target component from the plant material in liquid state (sunflower oil) is similar to that in solid state and includes both internal diffusion transfer of the component to the surface of the phase contact and the external diffusion from the surface to the bulk of fluid. The difference lies in determining the driving force of the process (speed) as noted above. Experimental studies of the kinetics of the target components extraction from plant material [5-10] showed that the speed of the process primarily depends on the state of the seeds (grinded or non-grinded), grain size, temperature, solvent properties, etc.

To establish the mechanism of target components extraction from plant materials and to determine the diffusion coefficient a more simple mathematical model

(Fig. 5) with an uniform separation of the target component (oil) can be used [5, 9]:

$$\ln \left( 1 - \frac{C_1}{C_f} \right) = \frac{3 \cdot K \cdot t}{R} \cdot \frac{C_{in}}{C_{in} - C_f} \quad (9)$$

where  $C_1$  is a concentration of oil in the bulk of the solution,  $\text{kg/m}^3$ ;  $C_f$  is a final concentration of oil in solution,  $\text{kg/m}^3$ ;  $C_{in}$  is an initial concentration of oil in grain,  $\text{kg/m}^3$ ;  $t$  is time of extraction, s.

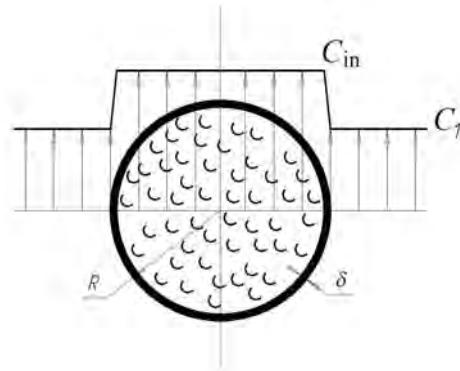
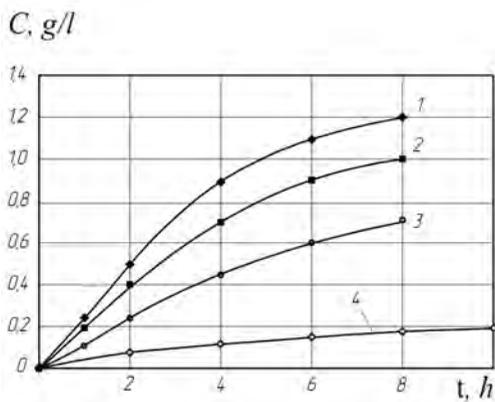


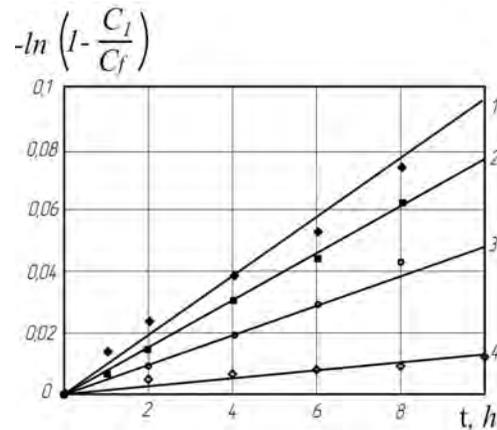
Fig. 5. The scheme of simplified physical model of the target components extraction from the seeds of plant material

Fig. 6a shows the kinetic dependence of the amaranth concentration on the time of extraction from various fractions of grinded and not grinded seeds, and in

Fig. 6b the dependence  $-\ln \left( 1 - \frac{C_1}{C_f} \right)$  on time.



a)



b)

Fig. 6. Kinetic dependence (a) and dependence  $-\ln \left( 1 - \frac{C_1}{C_f} \right)$  (b)

of oil extraction from various fractions of amaranth seeds ( $d_m$ , mm): 0.7 (1); 0.5 (2); 0.3 (3) and not grinded seed (4)

Eq. (9) in semi-logarithmic coordinates  $-\ln\left(1 - \frac{C_1}{C_f}\right) = f(t)$  is a straight line. According to the slope angle we determined the kinetic coefficient  $K$ .

$$\operatorname{tg}\alpha = \frac{3K}{R} \left( \frac{C_{in}}{C_{in} - C_f} \right) \quad (10)$$

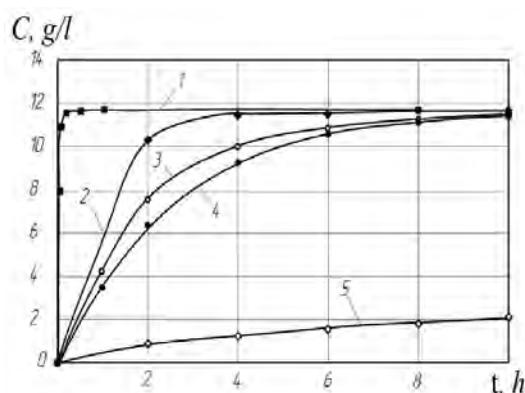
The verification of Eq. (9) was carried out on the basis of experimental studies of the kinetics of oil extraction from rapeseed, amaranth and others in a stirred apparatus and Soxhlet apparatus from grinded and not grinded seeds by *n*-hexane at the temperature of 313 K [5, 8-10, 15-19]. The kinetic coefficients  $K$  were determined (Fig. 6b):  $K_1 = 0.86$  m/h;  $K_2 = 1.5$  m/h;  $K_3 = 2.56$  m/h;  $K_4 = 3.62$  m/h.

The diffusion coefficient of not grinded rapeseed at the temperature of 313 K is  $5 \cdot 10^{-12}$  m<sup>2</sup>/s [5]. Thus, experimental investigations of the extraction kinetics from grinded seeds of rape, amaranth and others confirm the internal diffusion mechanism of the extraction process [5, 8-10].

For grinded seeds, the extraction process proceeds through a mixed mechanism of internal diffusion and external diffusion, since the barriers associated with the movement of the target component from the middle of the grain pores to the surface of phase contact are destroyed.

In this way, the seed grinding size determines the speed of the extraction process, since it depends on the mechanism of the extraction process. On the other hand, the increase in the grinding size is associated with increased energy costs, complication of the technological scheme of the process, the necessity of additional equipment, etc. Therefore, establishment of the most optimal grinding size, which determines the speed of this process for maximum removal of the target component, requires technical and economic calculations.

Thus, on the basis of studying the kinetics of target components extraction from comparatively large particles of mineral raw materials, as well as from the grinded seeds of plant material, the limiting step is internal diffusion. This is especially true during vegetable oil extraction from vegetable seeds, when the process takes several days (Figs. 6a and 7). Therefore, in order to accelerate the process, grinded seeds are used, as a result of which the barriers for the target component movement to the surface of phase contact are destroyed. At the same time, the surface of the phase contact of the seed increases. The influence of the raw material dispersion in the process of extraction on the kinetics of the process is shown in Figs. 6 and 7 when extracting oil from amaranth seed and amaranth hybrid [2, 8, 9] at different temperatures. Similar dependencies were obtained for extracting the target components from mineral raw materials (sulfur from ore).



**Fig. 7.** Kinetics of oil extraction from various fractions of grinded seeds of amaranth hybrid by methylene chloride in a device with a stirrer at 293 K:  $d_m = 0.08$  mm (1);  $d_m = 0.12$  mm (2);  $d_m = 0.3$  mm (3);  $d_m = 0.5$  mm (4) and not grinded seed (5)

The basis for method of establishing the kinetics of the target component extraction, taking into account the internal and external diffusion mechanism of extraction, the known equation is taken [2, 5]:

$$C = \frac{M_0}{W} \cdot \left[ 1 - \alpha \left( 1 - \frac{t}{T_p} \right) - (1 - \alpha) \left\{ \frac{1}{2} \pm \cos \left[ 60^\circ + \frac{1}{3} \arccos \left( \pm \left( 1 - 2 \frac{t}{T_e} \right) \right) \right] \right\}^3 \right] \quad (11)$$

In this equation, it is assumed that the entire set of grinded and separated fractions contains particles from which the oil is extracted by the external diffusion mechanism and particles from which the oil is extracted by the internal diffusion mechanism. Therefore, Eq. (11) takes into account the effect of seed dispersion on the kinetics of the process.

The mass of oil contained in the particles of the first kind is denoted as  $M_{01}$ , and the mass of oil contained in particles of the second kind – as  $M_{02}$ . The general mass is denoted as  $M_0$ :  $M_0 = M_{01} + M_{02}$

The ratio  $M_{01}/M_0$  is denoted by  $\alpha$ , taking into account that  $M_{01} = M_0 \cdot \alpha$ ;  $M_{02} = M_0 \cdot (1 - \alpha)$ .

For external diffusion dissolution  $\alpha = 1$  and for internal diffusion extraction  $\alpha = 0$ .

The mass of the oil contained in the particles of the first and second kinds were determined:

$$M_{01} = \frac{\pi d_0^3}{6} \cdot \rho_0 \cdot n \quad (12)$$

$$M_{02} = \frac{4\pi R^3}{3} \cdot \rho m \quad (13)$$

where  $\rho_0$  is oil density, kg/m<sup>3</sup>;  $n$  is the number of particles with oil on the surface;  $\rho$  is an amount of oil per unit of particle volume, kg/m<sup>3</sup>;  $m$  is the number of particles in the

pores of which there is oil;  $d_0$  is the initial diameter of the particle.

In the case of this assumption, the amount of oil present in the mixture at time  $t$  was determined by the equations:

$$M_1 = \frac{\pi d^3}{6} \cdot \rho_0 n \quad (14)$$

$$M_2 = \frac{4\pi r^3}{3} \cdot \rho \cdot m \quad (15)$$

Dividing Eqs. (12) and (13) by (14) and (15), respectively we received Eqs. (16) and (17):

$$M_1 = M_{01} \cdot \varphi_p^3 = M_0 \cdot \alpha \cdot \varphi_p^3 \quad (16)$$

$$M_2 = M_{02} \cdot \varphi_e^3 = M_0 \cdot (1 - \alpha) \cdot \varphi_e^3 \quad (17)$$

The amount of oil transferred to the solution at time  $t$  was determined from the equation of material balance:

$$M = M_0 - (M_1 + M_2) = M_0 \left[ 1 - \varphi_p^3 \alpha - (1 - \alpha) \varphi_e^3 \right] \quad (18)$$

On the basis of the above equations, the dependences for external diffusion dissolution and for internal diffusion extraction of vegetable oil were obtained:

$$1 - \varphi_p = \frac{t}{T_p} \quad (19)$$

$$1 - 3 \cdot \varphi_e^2 + 2 \cdot \varphi_e^3 = \frac{t}{T_e} \quad (20)$$

where  $\varphi_p$  and  $\varphi_e$  are dimensionless radii;  $\varphi_e = r/R$  in conditions of internal diffusion;  $R$  is the radius of not grinded grain;  $r$  is the radius of the sphere corresponding to the time  $t$ , limited by the presence of the target component in the grain;  $T_p$  is the time of complete dissolution of the target components;  $T_e$  is the time of complete removal of the target component under extraction conditions.

$$\varphi_p = 1 - \frac{t}{T_p} \quad (21)$$

$$\varphi_e = \frac{1}{2} \pm \cos \left[ 60^\circ + \frac{1}{3} \arccos \left( \pm \left( 1 - 2 \frac{t}{T_e} \right) \right) \right] \quad (22)$$

the sign “+” indicates that  $\frac{t}{T_e} \leq \frac{1}{2}$ , the sign “-“ indicates that  $\frac{t}{T_e} > \frac{1}{2}$ .

As is known, Eq. (11) describes the kinetics of compatible extraction (external and internal diffusion transfer mechanism) in the case of constant driving force ( $\Delta C = \text{const}$ ), when the final concentration is much smaller than the concentration of saturation ( $C_f < C_s$ ). This equation can be transformed for the conditions of compatible extraction with variable driving power  $\Delta C = \text{var}$  by changing the parameter  $\varphi_p$  in Eq. (18). To do this we use known differential equation of dissolution kinetics [11]:

$$-\frac{d\varphi_p}{dt} = \frac{2K\Delta C}{d_0\rho} \quad (23)$$

where  $K$  is a coefficient of mass transfer.

On the basis of this equation we obtained Eqs. (19), (20) and (22), which after transformations give us the final result in the following form:

$$C = \frac{M_0}{W} \cdot \left\{ 1 - \alpha \left[ 1 - A_i - t \left( \frac{1 - \varphi_{p_{i-1}} - A_i}{t_{i-1}} \right) \right]^3 - (1 - \alpha) \left[ \frac{1}{2} \pm \cos \left[ 60^\circ + \frac{1}{3} \arccos \left( \pm \left( 1 - 2 \frac{t}{T_e} \right) \right) \right] \right]^3 \right\} \quad (24)$$

Eqs. (11) and (24) can be used to study the influence of the dispersion of ore or plant material on the extraction mechanism at  $\Delta C = \text{const}$  and  $\Delta C = \text{var}$ , respectively.

For the experimental study of kinetics of compatible extraction, the results presented in Fig. 8 were used. For plant materials, the technique of experiments was the following: rapeseeds, amaranth hybrid and camelina were ground and separated into fractions with medium size  $d_m = 0.7, 0.5, 0.3$  and  $0.16$  mm. In each fraction, the oil content was determined. It was assumed that for the fraction with  $d_m < 0.3$  mm the oil extraction was carried out by the external diffusion mechanism. A sample of each fraction was put in a device with a stirrer, in which chloride methylene as an extractant was heated to the temperature of 313 K. At definite intervals, samples were taken and analyzed for the oil content by gravity method. The experiments were carried out at the constant speed  $n = 200$  rpm.

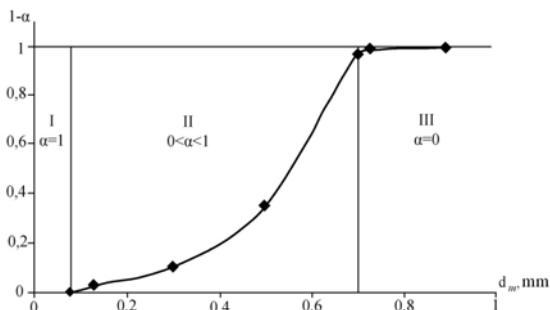
The similar experiments were performed for every fractions with a particles size  $d_m < 0.3$  mm.

To construct the dependence  $1 - \alpha = f(d_m)$ , the value of  $\alpha$  for each fraction was determined as follows: according to the predefined values of  $\alpha$  for each fraction and mixture, the theoretical curves for the extraction kinetics were calculated using Eq. (11). The value of  $\alpha$  for each fraction was taken according to the curve that most closely coincides with the experimental data.

The obtained values of  $\alpha$  for the fractions with  $d_{m1}, d_{m2}, d_{m3}, d_{m4}$  were  $\alpha_1 = 0, \alpha_2 = 0.2, \alpha_3 = 0.5, \alpha_4 = 1$ . The analysis of the data showed that the results of experimental studies satisfactorily adjust with Eq. (11), which allows us to recommend equations for predicting the extraction kinetics for different objects of oil extraction from plant raw materials at  $\Delta C = \text{const}$ . Additionally, it is possible to determine the optimal grinding size to achieve the most economical extraction process.

Fig. 8 shows the dependence  $1 - \alpha = f(d_m)$ , which characterizes the influence of the dispersion of the grinded seed of camelina on the extraction mechanism for the conditions  $\Delta C = \text{const}$ . The analysis of Fig. 8 showed that the extraction process for particles of grinded seeds with an average size of less than  $0.16$  mm occurs under the

external diffusion mechanism. For not grinded seeds, the process takes place exclusively by the internal diffusion mechanism. For the particles of the grinded seeds with  $0.16 \text{ mm} < d_m < 0.7 \text{ mm}$ , the internal diffusion extraction and external diffusion dissolution are characteristic.



**Fig. 8.** Influence of raw material grinding size on the degree of oil extraction, in the form of dependence  $1 - \alpha = f(d_m)$

Thus, this method makes it possible to study the effect of dispersion on the mechanism of the target components extraction from grinded and not grinded seeds, as well as experimentally determine the required grinding size that affects the energy consumption.

## 4. Conclusions

It was established that extraction processes of target components from porous solid-state structures are characterized by the presence of internal diffusion, external diffusion and mixed transfer mechanisms. The internal diffusion mechanism is the slowest one and determines the speed of the entire process.

The presence of internal diffusion mechanism is characteristic of large particles of mineral raw materials, from which the extraction of the target component and not grinded seeds of plant materials is carried out. For polydispersed particles, the extraction process is carried out according to mixed internal diffusion and external diffusion transfer mechanisms. It has been confirmed that for the extraction of target components which are in the porous skeleton in a solid state, the equilibrium is established when the concentration in the solution and in the porous skeleton is equal to the concentration of saturation; for the conditions under which the component is in a liquid state, the equilibrium occurs when the concentrations of the components in pores and in the bulk are aligned. It was shown that effective extraction from the polydispersed mixture would occur under conditions close to the external diffusion mechanism.

## References

[1] Semenyshyn Ye., Trotskyj, V., Fedorchuk-Moroz V. et al.: Visnyk Nats. Univ. "Lvivska Politehnika", 2008, **622**, 80.

- [2] Semenyshyn Ye., Tsiura N. Rymar T., Krvavych A.: Naukovi Zraci ONACT, 2016, **80**, 38.
- [3] Tepliakov Yu., Rudobashta S., Nechaev V., Klymov A.: Vestnik Tambomskogo Gos. Techn. Univ., 2009, **15**, 553.
- [4] Kaloshin Yu.: Tehnologiya i Oborudovanie Maslozhirovykh Predpriyatiy. Akademiya, Moskva 2002.
- [5] Semenyshyn Ye., Rymar T.: Visnyk Nats. Univ. "Lvivska Politehnika", 2017, **868**, 298.
- [6] Pavliuk I., Dyachok V., Novikov V., Ilkiv I.: Chem. Chem. Technol., 2017, **11**, 487. <https://doi.org/10.23939/chcht11.04.487>
- [7] Symak D., Atamanyuk V., Gumnytsky Y.: Chem. Chem. Technol., 2015, 9, 493. <https://doi.org/10.23939/chcht09.04.493>
- [8] Stadnyk R., Semenyshyn, Ye., Fedorchuk-Moroz V. et al.: Visnyk Nats. Univ. "Lvivska Politehnika", 2009, **644**, 162.
- [9] Semenyshyn Ye., Yatchyshyn Yo., Stadnyk R.: Khim. Promyslovist` Ukrainy, 2011, **4(105)**, 40.
- [10] Semenyshyn Ye., Ivashchuk O., Rymar T.: Visnyk Nats. Univ. "Lvivska Politehnika", 2018, **886**, 177.
- [11] Akselrud G.: Masoobmen v Sisteme Tverdoe Telo – Zhidkost. Izd. Lvovsk. Univ., Lvov 1970.
- [12] Lyuta O., Symak D.: Visnyk Nats. Univ. "Lvivska Politehnika", 2018, **886**, 165.
- [13] Dyachok V., Ilkiv I.: Chem. Chem. Technol., 2013, **7**, 27. <https://doi.org/10.23939/chcht07.01.027>
- [14] Symak D., Gumnytsky J., Atamaniuk V., Nagursky O.: Chem. Chem. Technol., 2017, **11**, 469. <https://doi.org/10.23939/chcht11.04.469>
- [15] Semenyshyn Ye., Stadnyk R., Andryyashcheva M., Psyuk Ya.: Visnyk Nats. Univ. "Lvivska Politehnika", 2015, **812**, 349.
- [16] Semenyshyn Ye., Stadnyk R., Onys'ko Kh.: Visnyk Nats. Univ. "Lvivska Politehnika", 2014, **787**, 337.
- [17] Petik P., Girman V., Mazur O.: Vostochno-Yevropejskyj Zh. Peredovykh Tekhnologiy, 2014, **6/6**, 13.
- [18] Krvavych A., Konechna R., Mylianych A. et al.: Voprosy Khimii i Khimicheskoi Tekhnologii, 2018, **5**, 111.
- [19] Semenyshyn Ye., Stadnyk R.: Visnyk Nats. Tekhn. Univ. "Kharkivskyj Politehnichnyy Instytut", 2011, **58**, 51.

Received: May 09, 2019 / Revised: May 12, 2019 / Accepted: October 14, 2019

## МАСООБМІН В СИСТЕМІ «ТВЕРДЕ ТІЛО-РІДИНА»: МЕХАНІЗМ ТА КІНЕТИКА ПРОЦЕСУ ЕКСТРАГУВАННЯ

**Анотація.** Вивчено механізм та кінетику вилучення цільових компонентів з мінеральної сировини (сульфур з сірчаної руди тетрахлоретиленом,  $Al_2O_3$  з бокситових спеків  $NaOH$ , міді з руди та малахіту хлорною кислотою), а також з олій (з амаранту, гібриду амаранту та рижію органічними розчинниками). Проведено експериментальні дослідження для підтвердження дифузійного характеру вилучення цільових компонентів з мінеральної сировини. Визначено коефіцієнти дифузії для мінеральних зразків. Встановлено, що вилучення цільового компонента з рослинної сировини відбувається внаслідок внутрішньої дифузійної передачі компонента до поверхні фазового контакту та зовнішньої дифузії від поверхні до об'єму рідини. Визначено кінетичні та дифузійні коефіцієнти для зразків рослинної сировини.

**Ключові слова:** кінетика екстрагування, система «тверде тіло-рідина», мінеральна сировина, рослинна сировина, цільові компоненти.