

Discrete diffusion during hydrolysis of keratin-containing raw materials with anisotropic internal structure

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Abstract. Dough making is a very critical stage of bread baking, largely, due to complex processes taking place thereupon. Key issues, undoubtedly, include a uniform distribution of liquid components over a generally anisotropic structure of the dough. Most solutions to the problem of uniform distribution of non-Newtonian liquids – protein-fat components of the dough, are based on the idea that the internal structure of particles is isotropic. However, it is not true in all cases. Some researchers have proved that distribution of fat components of different layers varies while the matter is being formed. A reason for it is a certain orientation and denser packing of protein molecules in the layers closer to kneading blades, which, naturally, means that the internal structure of different layers varies, too.

1 Introduction

In case of a stepwise depressurization when making aerated dough, for instance, a cellular structure of the outer layers of particles is destroyed by liquefied gases [1–4], so that their internal structure becomes obviously anisotropic.

Some studies [5–7] report that this multi-stage dough-kneading process is very effective, especially for confectionery products, where dough is deliberately saturated with air bubbles.

Let us indentify a mathematical model of discrete diffusion from spherical particles (corresponding to preparation of air bubbles) during a multi-stage dough-kneading under conditions of varying degree of destruction of the cellular structure; the particle has two zones with different diffusion coefficients: a core of undestroyed cells with diffusion coefficient D_1 and a surface layer made of destroyed cells with a larger diffusion coefficient D_2 . The matter repeatedly outflows from such two-zone particle (multi-stage kneading).

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2 Materials and methods

Mathematically, the problem can be formulated as the equation describing non-stationary diffusion

$$\frac{\partial c_{ij}^{(k)}}{\partial \tau} = D_k \left(\frac{\partial^2 c_{ij}^{(k)}}{\partial \tau} + \frac{2}{r} \frac{\partial c_{ij}^{(k)}}{\partial r} \right) \quad (1)$$

$$(\tau > 0, R_{k-1} < r_k < R_k, R_0 = 0)$$

under the boundary conditions:

$$C_{ij}^{(k)}(r, \tau_0) = f(r); \text{ where } \tau = 0, f(r) = C_0 = \text{const}; \quad (2)$$

$$C_{ij}^{(1)}(R_1, \tau) = C_{ij}^{(2)}(R_1, \tau) \quad (3)$$

$$-D_1 \frac{C_{ij}^{(1)}(R_1, \tau)}{\partial r} = -D_2 \frac{C_{ij}^{(2)}(R_1, \tau)}{\partial r} \quad (4)$$

$$\frac{\partial C_{ij}^{(1)}(0, \tau)}{\partial r} = 0; \quad C_{ij}^{(1)}(0, \tau) < \infty \quad (5)$$

$$C_{i1}^{(2)}(R_2, \tau) = C_n = \text{const} \quad (6)$$

$$\frac{\partial C_{i2}^{(2)}(R_2, \tau)}{\partial r} = 0; \quad C_0 > C_n. \quad (7)$$

Condition (2) is the initial condition that determines distribution of concentration of the mixed matter at the initial moment of the corresponding period.

Equations (3) and (4) are mathematical expressions of the boundary condition of the 4th kind, which determines equalities of concentrations and mass flows in case of a good mass-transfer contact between the core and the surface layer.

Expression (5) is a condition of symmetry and physical limitation of distribution of the mixed matter.

Conditions (6) and (7) are mathematical expressions for interaction of particles (air) with the environment in the first and second periods of the process. We will not lose generality of the problem statement even if $C_n=0$.

Therefore, formulation of this complex problem consists of several separate problems, each having an independent solution [10, 35, 36]. However, in this case, the problem seems much more complicated, as we consider diffusion of the matter in a two-layer particle with alternating continuous / discrete inflow of matter.

Applying methods of mathematical physics, we get a solution of the boundary value problem (1) - (7) which can be recorded, for a regular stage of the process and for average concentration values, as [8]:

$$\frac{c_0 - \bar{c}_{ij}^{(k)}}{c_0} = 1 + (-1)^j M_{ij}^{(k)}, \quad (8)$$

where,

$$M_{ij}^1 = 3k_D^m k_R^{n+1} \gamma_{11}^s \gamma^t (\sin \rho_{11})^{2-j} (\sin \gamma_{1j} - \gamma_{1j} \cos \gamma_{1j}) \frac{1 - \gamma^2}{\Psi_2(k_R)} \left[\frac{2\Psi_2(k_R) \sin \gamma_{11}}{(1 - \gamma^2)\varphi_{11}} \right]^i * \\ * \left[\frac{2 \sin \gamma_{11} \sin \gamma_{12}}{(1 - \gamma^2)\varphi_{12}} \right]^n \exp \left[- \left(\gamma_{1j}^2 Fo + \sum_{i=1}^J \sum_{j=1}^2 \gamma_{1j}^2 Fo_{ij} - \gamma_{1j}^2 Fo_{ij} \right) \right] ; \\ M_{ij}^2 = \begin{cases} \frac{\sin \gamma_{11} (\sin \rho_{11} + \sqrt{k_D} \gamma_{11} \cos \rho_{11} - \sqrt{k_D} \gamma_{11} k_R)}{\sqrt{k_D} (1 - k_R^3) \gamma_{11} \sin \rho_{11} (\sin \gamma_{11} - \gamma_{11} \cos \gamma_{11})} M_{11}^{(1)} & \text{where } i = j = 1 \\ \frac{\sqrt{k_D}}{1 - k_R^3} M_{ij}^{(1)} & \text{for the rest } i \text{ and } j \end{cases} ; \\ s = j - 3 + (k - 1)(2 - j); m = \frac{1}{2} [i + (-1)^j - (k - 1)]; \\ t = \begin{cases} i + (-1)^j & \text{where } i = 1; n = i + j - 2 \\ i + (-1)^j + 2 & \text{where } i > 1; \gamma = \frac{\gamma_{11}}{\gamma_{12}} \end{cases} .$$

Where γ_{11} is the first positive root of the characteristic equation

$$\sqrt{k_D} \gamma \text{ctg} \rho + 1 + k_D (\gamma \text{ctg} \gamma - 1) = 0 \quad (9)$$

γ_{11} - the first positive root of the characteristic equation

$$k_D (\gamma \text{ctg} \gamma - 1) (\sqrt{k_D} k_R \gamma \text{ctg} \rho - 1) + \rho \text{ctg} \rho - (k_D k_R \gamma^2 + 1) = 0 \quad (10)$$

$$\varphi_{11} = \sqrt{k_D} \gamma_{11} \sin^2 \rho_{11} + \rho_{11} \sin^2 \gamma_{11} + \frac{1 - k_D}{\sqrt{k_D} \gamma_{11}} \sin^2 \gamma_{11} \sin^2 \rho_{11} ;$$

$$k_D \left\{ \begin{aligned} & \frac{\varphi_{12}}{\varphi_{11}} = \\ & \left((\sin \rho_{12} + \sqrt{k_D} k_D \gamma_{12} \cos \rho_{12}) (\gamma_{12} - \sin \gamma_{12} \cos \gamma_{12}) + \right. \\ & \left. + \sqrt{k_D} \sin \gamma_{12} (\gamma_{12} \cos \gamma_{12} - \sin \gamma_{12}) (\cos \rho_{12} - \rho_{12} k_R \sin \rho_{12}) - \right. \\ & \left. - \gamma_{12} \sin^2 \gamma_{12} [k_R \rho_{12} \cos \rho_{12} + (k_R^2 + 1) \sin \rho_{12}] \right) \end{aligned} \right\} ;$$

$$\psi_2(k_R) = \sqrt{k_D} \gamma_{12} \sin \gamma_{12} \cos (\sqrt{k_D} \gamma_{12} (k_R - 1)) + \\ + [(1 - k_D) \sin \gamma_{12} + k_D \gamma_{12} \cos \gamma_{12}] \sin (\sqrt{k_D} \gamma_{12} (k_R - 1)) ;$$

i - the stage number ($i = 1, 2, 3, \dots, J$); j - the number of the stage period ($j=1,2$); k - a particle zone number ($k=1$ is the core, $k=2$ is the surface layer); c - concentration of diffusing matters;

$$k_D = \frac{D_1}{D_2} ; k_R = \frac{R_2}{R_1} ;$$

$$\rho = \sqrt{k_D}(k_R - 1)\gamma;$$

$$\sqrt{k_D}(k_R - 1) - \text{irrational number};$$

$$F_0 = \frac{D_1\tau}{R_1^2}; \quad F_{0ij} = \frac{D_1\tau_{ij}}{R_1^2} - \text{Fourier numbers.}$$

Thus, we have identified distribution of concentrations in each zone at any stage and any period. Using those results, we can estimate diffusion coefficients of real materials by zones, and, applying the interval calculation method, estimate a possible degree of destruction of the cellular structure of ingredients at each stage. An adequate analytical description of the stepwise dough-kneading process facilitates optimization of the process.

The model we received ensures analytical estimation of efficiency of discrete diffusion from two-zone spherical particles compared to continuous diffusion in case of multi-stage matter extraction, which can be presented as the inequation [9–10].

$$0 < A \leq 1, \quad (11)$$

where

$$A = -\frac{1}{2}k_D^{\frac{i+1}{2}}\gamma_{11}\gamma^3\frac{\varphi_{11}(1-\gamma^2)\sin\gamma_{12}-\gamma_{12}\cos\gamma_{12}}{\psi_2(k_R)}\frac{\left(\frac{2\sin\gamma_{11}}{(1-\gamma^2)}\right)^2\left[-\frac{k_R\gamma\psi_2(k_R)\sin\gamma_{12}}{\varphi_{11}\varphi_{12}}\right]^i}{*}\exp\left[-\sum_{i=1}^j\sum_{j=1}^2\gamma_{1j}^2Fo_{ij}-\gamma_{11}^2iFo\right]$$

$$Fo = \frac{D_1t}{R_1^2},$$

$$t = t_{dif} = t_{isol},$$

t_{dif} - time of proper diffusion (matter inflow) during the stage; t_{isol} - time of no-flow through the outer surface of a particle.

This approach can also be used when dividing a particle into an arbitrary number of zones with different internal structure.

Mixing and adsorption in the solid-liquid system, widely used in the food production industry, can be both considered in terms of mass transfer as processes with counter mass flows [11].

In the solid phase, the mixed matter usually consists of two elements: the one held by sorption forces, and the other – distributed, usually evenly, in the pore space. During sorption in the solid phase, the matter gets accumulated due to sorption itself and due to mixing in the pore space. Based on the above, we can formulate the problem as the one with an internal mass source, time-dependent and positive in cases of adsorption and mixing.

In general, the problem for spherical particles can be recorded as follows:

$$\frac{\partial C_1}{\partial \tau} = D\left(\frac{\partial^2 C_1}{\partial r^2} + \frac{2}{r}\frac{\partial C_1}{\partial r}\right) + a_c(\tau); \quad (12)$$

$$\tau > 0 ; 0 < r < R ;$$

$$C_2(R, \tau) = f(\tau, Y); \quad (13)$$

$$C_1(r, 0) = C_{10b} > C_{20} ; \quad (14)$$

$$C_1(r, 0) = C_{10b} < C_{20} ; \quad (15)$$

$$C_1(r, 0) = 0 ; \quad (16)$$

$$C_1(0, \tau) \neq \infty; \quad (17)$$

$$\frac{\partial C_1(0, \tau)}{\partial r} = 0 , \quad (18)$$

where C_1 , C_{10} are current and initial values of emulsion concentration inside the particles; C_2 , C_{20} - current and initial values of emulsion concentration outside the particles; τ - time; r - current value of the radius; R - radius of the sphere; a_c - rate of adsorption (desorption); Y - normal coordinate to the surface of the sphere.

Formula (14) relates to mixing, formulas (15) and (16) - to adsorption.

It should be noted that an adsorption isotherm is not included in the above-presented system, since the isotherm characterizes the equilibrium state, i.e., should be obtained from the solution as the limiting state of the system.

Conditions (14) - (16) relate to directions of mass flows during mixing and adsorption, (17) and (18) are well known. The function $a_c(\tau)$ shows a change in the adsorption (desorption) rate over time and, understandably, depends on the nature of absorption forces, value of the adsorbent specific surface, properties of the adsorbed matter, its concentration, and other sorption characteristics of the solid-liquid system. In case it is gases (vapors) that get adsorbed, sorption goes very quickly ($10^{-8} - 10^{-9}$ c), as shown in [12], while adsorption from an emulsion lasts dozens of minutes; by order of magnitude it is equal to the duration of real diffusion processes. As for desorption during mixing, there are cases [13] when desorption takes longer than mixing. So, for the solid-liquid system

$0 \leq a_c(\tau) \leq a_{ir}$, where $0 \leq a_{ir} < \infty$ (a_{ir} is the initial adsorption rate); thus, it is necessary to determine the form of the function. The choice is narrow: among all functions that can be used to solve the system (12)-(18), only the cosine functions, the exponential function, and the Gaussian function meet the conditions; the last two functions require experimental identification of their coefficients, but their curve forms differ little from the cosine function. Given the aforesaid, the equation will look as:

$$a_c(\tau) = a_{hc} \cos \frac{\pi}{2} \frac{\tau}{\tau_{fc}} , \quad (19)$$

where τ_{fs} is the final time of sorption.

The boundary condition (13) for the counter-flow, which is practically very important, is proposed to be:

$$C_2(R, \tau) = C_{20} + (C_{2k} - C_{20}) \sin \frac{\pi}{2} \frac{\tau}{\tau_k} \pm \delta \frac{dC_2(Y, \tau)}{dY} , \quad (20)$$

where C_{2k} is final concentration of the outer emulsion; τ_k is final time of the whole process; δ - is thickness of the boundary layer; the plus sign refers to mixing, and the minus sign refers to adsorption.

3 Results

In case $C_{2k}=0$ and $\delta = 0$, the function is similar to changes in concentration of the emulsion C_2 depending on time τ in industrial mixers (Fig. 1) and, compared to other functions, has the same benefits as function (19).

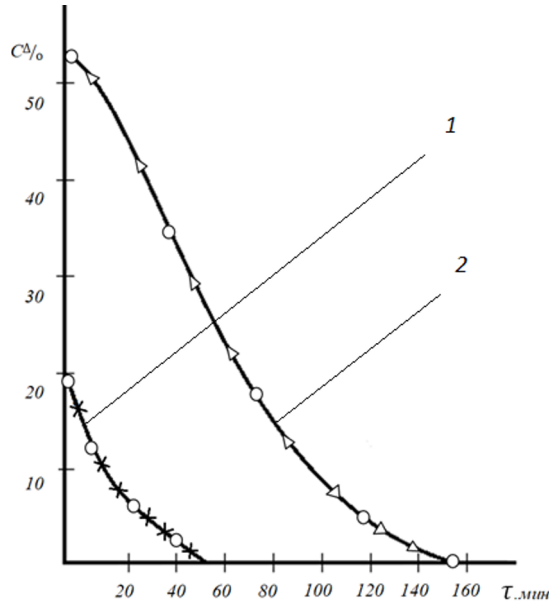


Fig. 1. Dependence of protein-fat emulsion concentration on time in industrial devices: 1 – ribbon mixer; 2 – blade mixer.

The third term of the function (20) relates to a boundary layer on the sorbent surface. The third term in condition (20) substantiates the condition. For instance, in case of adsorption at $\tau \rightarrow 0$, $C(R,0) \rightarrow 0$, which meets condition (16); while if there were no third term in condition (20), $C_2(R,0) \rightarrow C_{20}$.

The latter argument can be explained, in particular, by the fact that under certain hydrodynamic conditions $\delta \rightarrow 0$. Finally, the third term brings condition (20) in compliance with the experiment by a correct selection of function $C_2(Y,\tau)=f(Y)$. In case $\tau \rightarrow \infty$ $C_2(R,\infty) \rightarrow C_{2k} \rightarrow C_{20}$, since concentration gets leveled off by the boundary layer thickness, i.e. $\frac{dC_2(Y,\tau)}{dY} = 0$.

Formulation of the problem might be made more complex by introducing boundary conditions of the third kind, but it would only lead to additional factoring of convective mass transfer, which is well known and presents little importance for modern intensified processes of mixing and adsorption.

The problem can be solved by the operational method, and after averaging can be recorded as:

$$\bar{C}_1(\tau) = C_{10} + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5, \quad (21)$$

$$\alpha_1 = -\sum_{n=1}^{\infty} \frac{6 \left\{ \frac{(\mu_n^4 + Pd_k^2)(\mu_n^4 + Pd_{kc}^2)(C_{20} - C(r, 0) \pm \delta \frac{dC_2(Y, \tau)}{dY}) -}{- \mu_n^2 [Pd_k(\mu_n^4 + Pd_{kc}^2)(C_k - C_{10}) - 4a_{kc}\tau_{kc}Pd_{kc}(\mu_n^4 + Pd_k^2)]} \right\} e^{-\mu_n^2 Fo}}{\mu_n^8 + \mu_n^4 (Pd_k^2 + Pd_{kc}^2) + Pd_k Pd_{kc}^2}; \quad (22)$$

$$\alpha_2 + \alpha_3 = \frac{3(C_{1k} - C_{10})}{\sqrt{Pd_k}} \left[\left(A + \frac{\sqrt{2}}{\sqrt{Pd_k}} \right) \cos Pd_k Fo + B \sin Pd_k Fo \right]; \quad (23)$$

$$A = \frac{sh \sqrt{\frac{Pd_k}{2}} ch \sqrt{\frac{Pd_k}{2}} + \sin \sqrt{\frac{Pd_k}{2}} \cos \sqrt{\frac{Pd_k}{2}}}{ch^2 \sqrt{\frac{Pd_k}{2}} - \cos^2 \sqrt{\frac{Pd_k}{2}}}$$

$$B = \frac{sh \sqrt{\frac{Pd_k}{2}} ch \sqrt{\frac{Pd_k}{2}} - \sin \sqrt{\frac{Pd_k}{2}} \cos \sqrt{\frac{Pd_k}{2}}}{ch^2 \sqrt{\frac{Pd_k}{2}} - \cos^2 \sqrt{\frac{Pd_k}{2}}} \quad (24)$$

$$\alpha_4 + \alpha_5 = -\frac{3a_{kc}\tau_{kc}}{2\pi Pd_{kc}} \frac{(sh^2 x \cos^2 x + ch^2 x \sin^2 x - 1) \left[\frac{(xchx \cos x - xshx \sin x - shx \cos x) \cos z -}{-(xchx \cos x + xshx \sin x - chx \sin x) \sin z} \right]}{sh^2 x \cos^2 x + ch^2 x \sin^2 x}; \quad (25)$$

where $x = \sqrt{\frac{Pd_{kc}}{2}}$; $z = Pd_{kc} Fo$;

$$\mu_n = n\pi; Pd_k = \frac{\pi R^2}{2D\tau_k}; Pd_{kc} = \frac{\pi R^2}{2D\tau_{kc}}; Fo = \frac{D\tau}{R^2};$$

Pd_k and Pd_{kc} are the Predvoditelev's criteria for the whole process and for sorption; Fo is the Fourier number.

It is necessary to remark that in case of counter-current processes $\tau_{ao} = \tau_{ek}$, $\tau_{ao} = \tau_{eo}$, where the “a” index refers to adsorption, the “e” index refers to mixing.

With $\tau_a \rightarrow \infty$ ($\tau_e \rightarrow 0$) the solution (21) can be transformed into

$$\bar{C}_{1a}(\infty) = \bar{C}_{1a}(0) = C_{10} - \frac{3a_{kc}\tau_{kc}}{2\pi Pd_{kc}} \frac{(sh^2 x \cos^2 x + ch^2 x \sin^2 x - 1) \left[\frac{(xchx \cos x - xshx \sin x - shx \cos x) \cos z -}{-(xchx \cos x + xshx \sin x - chx \sin x) \sin z} \right]}{sh^2 x \cos^2 x + ch^2 x \sin^2 x}. \quad (26)$$

The second term in this equation is the limiting concentration C_n as a result of sorption, or the concentration of the sorbed matter in the solid phase at $\tau_e = 0$. It can be reached at $\tau_a = \tau_{ks}$ or can be contained in the solid phase at $\tau_e = 0$ and further remains unchanged.

Therefore, $z = Pd_{kc} Fo_{kc} = \pi/2$ and then

$$\bar{C}_{1a}(\infty) = \bar{C}_{1a}(0) = C_{10} + C_n, \quad (27)$$

where

$$C_n = - \frac{3a_{HC}\tau_{KC}}{2\pi P d_{KC}} \frac{(sh^2x \cos^2 x + ch^2x \sin^2 x - 1)(xchx \cos x + xshx \sin x - chx \sin x)}{sh^2x \cos^2 x + ch^2x \sin^2 x}. \quad (28)$$

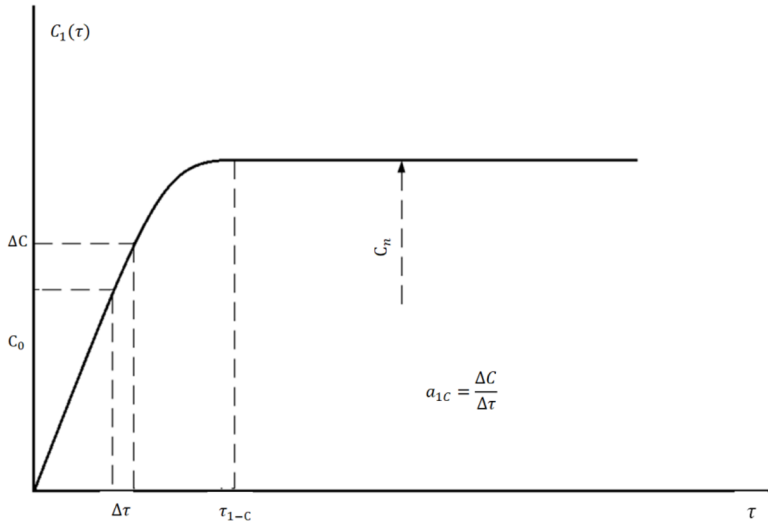


Fig. 2. Identification of limiting concentration of the sorbed matter.

Knowing D , taking τ_{ks} and a_{ns} from Figure 2 obtained from experimental data, we will determine C_n , and, hence, the limiting adsorption.

$$a_n = \frac{m}{\rho} C_n, \quad (29)$$

where m is the sorbent porosity.

Equation (28) can be easily used to get a transcendental equation in order to determine the internal diffusion coefficient.

$$D = \frac{\pi^2 R^2 C_n}{3a_{HC}\tau_K^2 F}, \quad (30)$$

where

$$F = \frac{(sh^2x \cos^2 x + ch^2x \sin^2 x - 1)(xchx \cos x + xshx \sin x - chx \sin x)}{sh^2x \cos^2 x + ch^2x \sin^2 x}.$$

4 Conclusion

A simple balance with result (27) leads to the initial equation for an adsorption isotherm in the counter-current process

$$a(\infty) = \frac{1}{\rho V_c} (V_{p0} C_0 - V_{\rho k} C_k) \quad (31)$$

or for adsorption

$$a_n = \frac{1}{\rho V_c} [C_0(V_{p0} - mV_c) - V_{pk}C_k], \quad (32)$$

where V_c, V_{p0}, V_{pk} are volumetric flow rates of the sorbent, emulsion at the entry and exit of the mixer; ρ - is density of the sorbent.

The adsorption isotherm curve is identified by dependence of $a(\infty)$ and a_n on a_{ns}, τ_{ks} and Pd_{ks} in accordance with equation (28); it should be kept in mind that a_{ns} , in its turn, depends on C_{10} .

References

1. I. E. Shabanov, Proceedings of the Voronezh State University of Engineering Technologies **2**, 43-47 (2012) DOI: 10.20914/2310-1202-2012-2-43-47
2. M. Marić, A. N. Grassino, Z. Zhu, et al., Trends Food Sci. Technol **76**, 28–37 (2018) DOI: <https://doi.org/10.1016/j.tifs.2018.03.022>
3. N. G. Kulneva, M. V. Zhuravlev, Proceedings of the Voronezh State University of Engineering Technologies **1**, 191-194 (2015) DOI:10.20914/2310-1202-2015-1-191-194
4. S. Liu, X. Shi, L. Xu, and Y. Yi, Chinese Journal of Oceanology and Limnology **34** (2), 372-381(2016) DOI:10.1155/2017/5898594
5. V. V. Beloborodov, Basic processes for the production of vegetable oils (Food Industry, Moscow, 1966)
6. S. Riaz, M. T. Sultan, I. S. Kosenko, et al., Journal of Microbiology, Bio-technology and Food Science **8**, 745–750 (2018) DOI:10.15414/jmbfs.2018.8.1.745-750
7. S. I. Niftaliev, O. A. Kozaderova, and K. B. Kim, Journal of Electroanalytical Chemistry **794**, 58-63 (2017) DOI: 10.1016/j.jelechem.2017.03.046
8. K. Yu. Muravev, N. V. Barakova, Proceedings of the Voronezh State University of Engineering Technologies **80** (3), 212-219 (2018) DOI:10.20914/2310-1202-2015-1-191-194
9. V. M. Bolotov, E. V. Komarova, E. S. Filatova, and V. V. Khripushin, Plant Chemistry **1**, 127-134 (2016) DOI: 10.14258/jcprm.201601860
10. G. V. Alekseev, A. A. Khripov, Journal of Food Process Engineering **38** (1), 11-18 (2015)
11. G. V. Alexeev, V. N. Krasilnikov, M. S. Kireeva, and E. V. Egoshina, International Food Research Journal **22** (3), 1156-1162 (2015)
12. S. Spînu et al., IOP Conf. Ser.: Mater. Sci. Eng. **877**, 012058 (2020)
13. M. S. M. Sharizan et al., IOP Conf. Ser.: Earth Environ. Sci. **36**, 012045 (2016)