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ULTRAFILTRATION CONCENTRATING OF CURD WHEY AFTER ELECTROFLOTATION TREATMENT

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Abstract: This work offers a view on the outcomes of a study focusing on ultrafiltration of curd whey treated on the basis of the membrane electroflotation method in order to ensure more complete extraction of whey proteins when processing recoverable dairy crude. The feature that makes the method different is the presence of membranes between the anode and the cathode while the machines for membrane electroflotation are designed so that current does not run through the whey. To determine the element composition of whey prior to and after electroflotation the method of electron probe X-ray microanalysis was used. It has been shown that the filtration rate of whey treated through electroflotation nearly doubles up if compared to the initial rate. There has also been detected the dependence related to the impact that the concentration of solids and the pressure have on the filtration rate; besides, the kinetics of the ultrafiltration process has been investigated. The method of electron probe X-ray microanalysis was employed to study the element composition of whey both before and after the electroflotation treatment. The increase in the whey ultrafiltration rate after electroflotation can be explained by a growing Hydrogen index and a reduced concentration of Calcium after electroflotation. Besides, a quantitative physical model of whey ultrafiltration was developed, which takes into view specific features of polarization layer formation. The model implies conditional division of whey flow at the membrane surface into two streams – a normal one and a tangential one. Part of the protein molecules transported by the normal flow settles on the membrane surface while the other part of them remains near the surface up until it is pushed into the whey bulk by protein molecules of the tangential flow. That all mentioned above fixes certain elements of newness in the field of membrane technologies. The study was performed at the Voronezh State University of Engineering Technologies and the North Caucasus Federal University (Russian Federation).

Keywords: Whey, ultrafiltration, electroflotation, membrane technology

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INTRODUCTION

Membrane technologies are the basis for low-waste and even non-waste (in case proper arrangements are made) dairy productions [1]. However, their wide implementation is limited, in particular due to low production capacity of membrane machines.

This also holds true for ultrafiltration separation of protein from milk whey [2]. Intensification of this process takes, first of all, minimization of protein deposit on the membrane surface. For instance, preliminary treatment of heated whey with ultrasound will reduce the membrane congestion and the amount of the protein deposit [3]. However, after numerous regular cleanings membranes increase their hydrodynamic resistance, which must be due to the fact that the pores get stuffed with protein from the inside surfaces [4].

If the impact of protein deposit could be minimized in any way, then concentration polarization will be the factor limiting the permeate flow through the membrane [5]. Thus, if for filtering sheep cheese whey membranes are used that are made of composite fluoropolymer, this allows a larger flow of permeate compared to polysulfone membranes, and protein deposits are minimum, while the dependency between the filtration rate

and the pressure is typical of concentration polarization [6].

Whey acidity has a significant impact on the degree of protein deposit. The major role in reducing membrane permeation in case of changing pH belongs, obviously, to β-lactoglobulin. This is suggested with the following experimentally obtained data. In the pH range of 3.9–4.65, the filtration capacity goes down along with the growing pH [7]. At the same time, there is data [8] showing that under a decreasing hydrogen index down to pH 4.65, a high concentration and a low ionic strength of the solution, the solubility of β-lactoglobulin goes down sharply. The results obtained through scanning electron microscope investigation [9] suggest that filtration of β-lacto-globulin solutions leaves the membranes with some deposit appearing as thick layers. Transmission electron microscopy of membrane cross section [10] shows that similar deposits with incorporations of α-lactalbumin globules are also to be found in case of milk whey filtration. The pH range where the whey filtration rate is minimum (pH 4.6–5.5) is close to the range where isoelectric points of various β-lacto-globulins can be found (pI 4.9–5.4) [11, 12].

Since the pH of curd whey lies within this range, its ultrafiltration is more complicated than that of cheese whey. Neutralization of cheese whey with correcting chemical agents in most cases results in its reduced organoleptic features and increased allergenic capacity [13].

This is why there is a lot of interest taken in reducing curd whey acidity with electrophysical methods, e.g. electrodialysis [14] or membrane electroflotation. Membrane electroflotation is different from conventional electroflotation used for protein-containing solutions by the presence of a membrane between the cathode and the anode, while the machines themselves are arranged so that the electric current does not go through whey. Treatment this way improves the product's organoleptic features, while the hydrogen index goes up as well [15].

Electroflotation results in 20–30% of protein eliminated from whey. One of the areas for using floated whey could be ultrafiltration treatment aiming at more thorough extraction of proteins. This is what the present work is focused on.

OBJECTS AND METHODS OF STUDY

In the ultrafiltration device used for the experiment, retentive mechanism/block moves round. There were track-etched polyethylene tetraphtalate membranes used, with a pore diameter of 60 nm. The filtration rate of distilled water in the ultrafiltration cell was 12 ml/min (pressure – 0.2 MPa) (filtration rate her means the volume of filtrate that has passed through the membrane as per a single unit of time). The required level of pH, while the samples of whey were prepared, was reached through adding NaOH or HC1.

For electron probe X-ray microanalysis the whey was first dried, after which scanning electron microscopy was used to select several areas (0.2 mm) within the obtained powders for further microanalysis.

EXPERIMENT OUTCOMES

For 10 minutes following electroflotation, the whey pH goes up from 5.0 to 6.05. The filtration rate of whey that has been treated this way nearly doubles if compared to untreated whey (Fig. 1).

Further electroflotation whey treatment would not increase the filtration rate any more. The results obtained through the experiment indicate that there is a certain value in ultrafiltration of floated whey as well as in further research in the area.

Fig. 2 shows the dependence of curd whey filtration rate on the dry substance concentration, measured under pH = 4.8 and pH = 6.6. The charts demonstrate that the filtration rates at pH close to the values in Fig. 1 reveals a difference of 1.7 times.

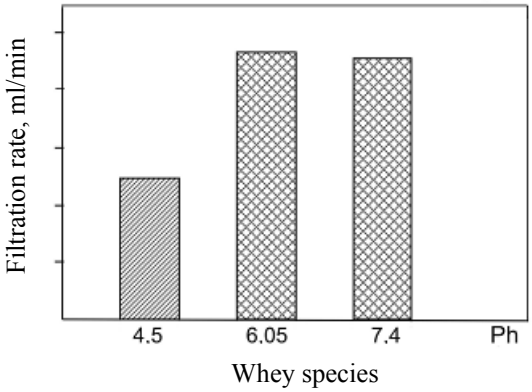

Fig. 1. Filtration rate for initial (pH = 4.5) and floated (pH = 6.05 and pH = 7.4) wheys (t = 30°C, p = 0.2 MPa).

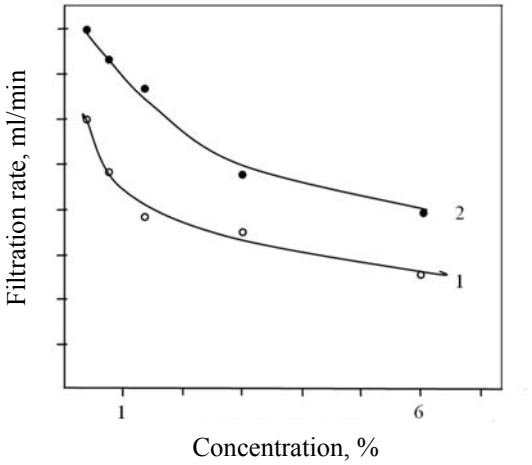

Fig. 2. Relationship between curd whey filtration rate and concentration of dry substances: (1) pH = 4.8; (2) pH = 6.6.

Therefore, the filtration rate growth for the floated whey, if compared to the initial whey, is mostly due to a significant change in the whey hydrogen index through electroflotation. The smaller angles in the charts at 3–6% concentrations of dry substances mean that the 10–15% reduction in the protein concentration in the floated whey, if compared to the initial whey, has virtually no impact on the filtration rate. Therefore, it is most likely that there are two factors

that have an impact on the growth in the floated whey filtration rate. This, first of all, is due to the changing values of pH, while there is some extra impact added by the reducing concentration in Calcium ions.

Calcium ions present in whey are known to speed down its filtration rate [16]. Electron probe analysis done on the whey prior to, and following electroflotation showed a decrease in the Ca ion concentration in the floated whey (Table 1).

Table 1. Whey element composition

Type of whey	Element, share,%				
	Na	P	Cl	K	Ca
Floated whey	1.25	0.43	1.55	0.57	0.52
Non-floated whey	1.06	0.8	1.03	0.45	1.02

The difference in the filtration rate for wheys with various pH value remains in case of changing share of the dry substances in the solution, which should also be true for floated and non-floated wheys. With dry substances concentration tending towards zero, the graphs, as could be expected, tend to intersect. Figures 3 and 4 demonstrate the dependence of filtrate volume on time, and filtration rate on pressure, respectively.

RESULTS AND DISCUSSION, PROCESS MODEL

Fig. 3 shows that 20–30 seconds after filtration is started, the curve indicating the dependence between filtrate volume and time reaches the straight line portion, which means stable filtration rate.

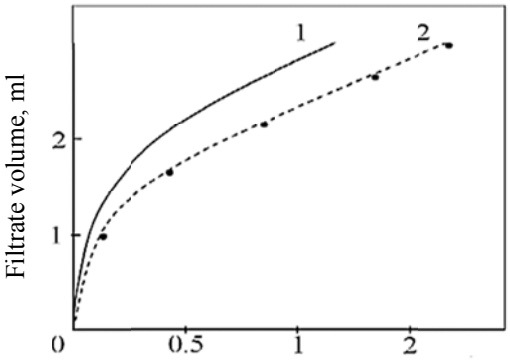

Fig. 3. Theoretical (1) and experimental (2) dependencies of filtrate volume of filtration time.

The grades of the curves were used to determine the rate of steady filtration. At pH = 4.0 the steady rate was v_{st} = 0.7 ml/min; at pH = 10 v_{st} = 1.2 ml/min. Since the process stabilization time is much lower than that of measuring (5 min) in the previous experiments then the average filtration rate determined through these experiments can be considered close to the stable rate. Using the data of the electron microscopy [10] we can suggest that the sublayer with the α-lactalbumin globules coating it, as well as the β-lactoglobulin layer above that, are developed within 20–30 sec.

Therefore, there is proof to the hypothesis stated in [11] and stating that globular formations of α-lact-albumin, casein, and immunoglobulins may deposit on the membrane shaping some sort of bridges above pores, which later on host proteins that can develop layers.

The data obtained make it possible to assume that jellification process in a thick layer of β-lactoglobulin follows a mechanism that is different from, for instance, jellification in rather concentrated protein solutions. Actually, the induction period of jellification in the latest case is from several hours to several days, while it only takes dozens of seconds for gel to develop on a membrane.

This means that polarization layer development could be viewed not from the stance of gel formation yet similarly to particle deposition on solid bodies from gas phase, or in case of sedimentation deposition, from a liquid under the conditions of a tangential flow.

Let us make a conditional division breaking the flow of protein molecules approaching the membrane surface in two – a flow that is normal towards the membrane surface and a tangential one.

Each molecule of the normal flow, when approaching the surface, will stay there for a certain period of time τ_0, until a connection develops between this molecule and other protein molecules. If, within this time, the molecule experiences an impact with a tangential flow molecule then it will be knocked out; however, if this impact takes place after the time of τ_0 then it will get fixed on the surface and will not be knocked out. This metastable condition of a molecule may take place during filtration, unlike other processes of interaction between solutions and solid bodies, due to the fact that a large protein molecule will pressed against the surface with the water flow passing through the membrane.

Let us accept that each molecule of the tangential flow experiences a co-impact with a molecule from the normal flow, so the number of these molecules N_τ approaching a certain point at the surface within the time of t shall be equal to the number of the co-impacts N_c within the same period of time:

$$N_c = N_\tau . \quad (1)$$

Then, all the molecules of the perpendicular flow would approach the same point on the surface in a certain average piece of time t_1 that depends on the solution concentration and the velocity of the molecules v_e:

$$t_1 = \frac{1}{v_e \sqrt[3]{C_0}} . \quad (2)$$

Since we are focusing on a thin layer of the liquid at the membrane surface, the concentration of C_0 in that might be taken as stable.

The period of time t_2, within which the tangential flow molecules reach point A, shall be expressed the following way:

$$t_2 = \frac{1}{v_\tau \sqrt[3]{C_0}}. \quad (3)$$

Within time t the point A will be reached by the N_{cross} number of cross flow molecules:

$$N_{cross} = \frac{t}{t_1}, \quad (4)$$

as well as by those of the tangent ail flow N_t:

$$N_\tau = \frac{t}{t_2}. \quad (5)$$

Now let us calculate the number of the molecules remaining on the surface as a result of impacts:

$$N_{rem} = N_{cross} - N_i \cdot P, \quad (6)$$

where P is the probability of an approaching molecule to be knocked out. Assume that within the time t_2, there were 10 molecules of the normal consequently approaching the boundary between impacts. The time for staying at the boundary for the first molecule is $10t_1$, $2^{nd} - 9t_1$, the last one – t_1. Let us take $\tau_0 = 3t_1$. In this case the tenth, the ninth, and the eighth molecules may be knocked out at impact, while the others may not. The knock out probability P is:

$$P = \frac{3}{10} = \frac{3t_1}{10t_1} = \frac{\tau_0}{10t_1}. \quad (7)$$

Since 10 is the number of the molecules that approached the boundary within a time interval between the impacts, then:

$$10 = \frac{t_2}{t_1}, \quad (8)$$

$$P = \frac{\tau_0}{t_2}. \quad (9)$$

In case the polarization layer is mostly developed faster than steady protein distribution takes place in the boundary layer, then the cross velocity of protein molecules v_e shall be approximately equal to the velocity of the filtrate flow passing through the membrane v_f.

Using (2), (3), (4), (5), (9) in (6), in view of $N_i = N_\tau$ we shall get:

$$N_{rem}(t) = t\left(v_f(t)\sqrt[3]{C_0} - \frac{\tau_0}{t_2^2} \right). \quad (10)$$

The developing polarization layer shapes, on the membrane surface, another membrane, through which whey is filtered.

In view of the hydraulic resistance and the membrane porosity, the Kozeny–Carman equation [17] could be modified as follows:

$$v_f = \frac{\varepsilon_m k_0 \cdot P}{a_1 + l}, \quad (11)$$

where is the coefficient k_0 depends on the filtrate viscosity, the microstructure and porosity of the polarization layer, ε_m is the membrane porosity, a_1 is the parameter taking into account its hydraulic resistance.

Joining the polarization layer thickness l with the number of protein molecules that constitute it, we will have the following formula:

$$l = \frac{m_\mu N_{rem}}{\rho_{pr}\left(S - S_{por}\right)}, \quad (12)$$

Where S is the area of the polarization layer, S_{por} is the total area of the pores that can be determined from the porosity of the polarization layer, m_μ is the mass of a protein molecule, N_{rem} is the number of protein molecules, and ρ_{pr} is its density.

Solving the equation system (10–12) regarding υ_f in view of (3) we shall get:

$$v_f = \frac{k_1 p}{\left[\frac{-(c + k \cdot v_\tau^2 \cdot t) + \sqrt{\left(c + k \cdot v_\tau^2 \cdot t\right)^2 - 4t\left(k \cdot v_\tau^2 \cdot c - k_1 p\right)}}{2} \right] + c}. \quad (13)$$

Here

$$k = \sqrt{C_0^{\,3}} \cdot \tau_0^2, \; k_1 = \varepsilon_m \cdot k_0, \; c = \frac{a_1 \cdot \rho_{pr}\left(S - S_{por}\right)}{m_\mu}.$$

The formula below could be used to calculate the volume of the filtrate developing within the time t:

$$V_f = \int_0^t \frac{k_1 \cdot p \cdot dy}{\left[\frac{-\left(c + k \cdot v_\tau^2 \cdot y\right) + \sqrt{\left(c + k \cdot v_\tau^2 \cdot y\right)^2 - 4y\left(k \cdot v_\tau^2 \cdot c - k_1 \cdot p\right)}}{2} \right] + c}. \quad (14)$$

The dependence of the filtration rate on the pressure, as calculated following the formula (13), as well as the kinetic curve determined through integration of this formula, lay within satisfactory agreement with the experimental ones (Fig. 3, 4). More accurate data could be obtained taking into account the specific hydrodynamic features of whey flowing through a canal of a certain shape.

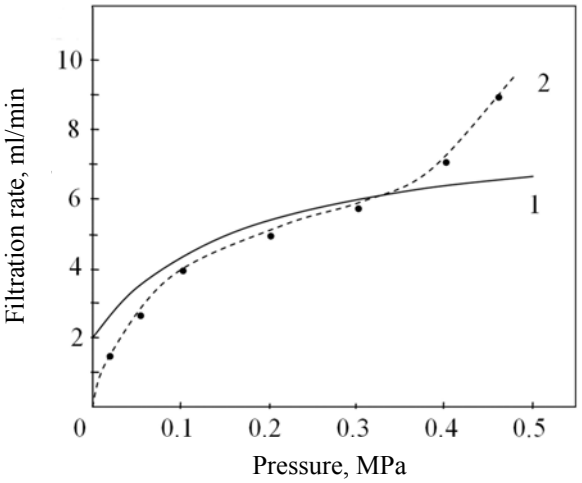

Fig. 4. Theoretical (1) and experimental (2) dependencies of filtration rate on pressure.

Let us accept that, following [18], the major role in β-lactoglobulin molecular interaction belongs to hydrophobic and electrostatic interactions, which may result in aggregation of proteins based o the mechanism described, for instance, in [19]. During that, the electrostatic interactions among protein globules are of local nature [20]. Then the condition for a molecule's getting fixed in the polarization layer will imply three events coming simultaneously – a position of a proper molecule that would ensure its touching the polarization layer with the hydrophobic area; the presence of a hydrophobic area on such a molecule at the spot of contact with the polarization layer, and not very strong an electrostatic repulsion between the areas of globules approaching one another. In case the pH of the solution is high enough, then the last condition often fails to be met, the time τ_0 gets longer and, respectively, following (13), (14) the filtration rate is growing, which is observed in case of floated whey filtration. Electroflotation treatment for curd whey, which leads to a growth in the protein molecule negative charge, is likely to prove especially useful when using negatively charged membranes [21] that improve significantly ultrafiltration productivity. Due to a lower level of Ca in concentrates of curd whey after it has been subjected to electroflotation treatment, they can be recommended to elderly people, since milk and dairy products may have a negative effect on the health in the elderly age, that is due to specific features about calcium absorption, which facilitates atherosclerosis [22].

CONCLUSION

The study has shown that there is a reason to conduct ultrafiltration concentration of curd whey after it has been subjected to electroflotation treatment.

Improved organoleptic properties of floated whey allow using ultrafiltration not only to produce whey protein concentrates with a high concentration factor, yet also to make base for yogurt, dairy drinks, and jellies with a higher content of whey proteins. At the same time it is possible not to exceed the concentration factor of 2–2.5, which reduces the load on the ultrafiltration equipment and decreases its elements, membranes first of all, contamination with protein.

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REFERENCES

1. Khramtsov A.G. *Fenomen molochnoy syvorotki* [Milk whey phenomenon]. St. Petersburg: Professija Publ., 2011. 804 p.
2. Evdokimov I.A., Zolotareva M.S., Volodin D.N., et al. Efficient technologies for acid milk whey processing. *Molochnaya promyshlennost'* [Dairy industry], 2007, no. 11, pp. 95–96. (In Russian).
3. Koh Li Ling A., Nguyen Hanh Thi Hong, Chandrapala Jayani, et al. The use of ultrasonic feed pre-treatment to reduce membrane fouling in whey ultrafiltration. *Journal of Membrane Science***,** 2014, vol. 453, pp. 230–239. DOI: https://doi.org/10.1016/j.memsci.2013.11.006.
4. Berg Thilo H.A., Knudsen Jes C., Ipsen R., et al. Investigation of consecutive fouling and cleaning cycles of ultrafiltration membranes used for whey processing. *International Journal of Food Engineering*, 2014, vol. 10, no. 3, pp. 321–325.
5. Williams P.S., Giddings S.B., and Giddings J.S. Calculation of flow properties and end effects in field-flow fractionation channels by a conformal mapping procedure. *Analytical Chemistry,* 1986, vol. 58, no. 12, pp. 2397–2403. DOI: DOI: 10.1021/ac00125a010.
6. Macedo A., Duarte E., and Pinho M. The role of concentration polarization in ultrafiltration of ovine cheese whey. *Journal of Membrane Science*, 2011, vol. 381, no. 1–2, pp. 34–40. DOI: 10.1016/j.memsci.2011.07.012.
7. Konrad G., Kleinschmidt T., and Faber W. Ultrafiltration flux of acid whey obtained by lactic acid fermentation. *International Dairy Journal*, 2012, vol. 22, no. 1, pp. 73–77. DOI: 10.1016/j.idairyj.2011.08.005.
8. Díaza O., Pereira C.D., and Cobos A. Functional properties of ovine whey protein concentrates produced by membrane technology after clarification of cheese manufacture by-products. *Food Hidrocolloids*, 2004, vol. 18, no. 4, pp. 601–610. DOI: 10.1016/j.foodhyd.2003.10.003.

9. Lee D.N. and Merson R.L. Examination of cottage cheese whey proteins by scanning electron microscopy relationship to membrane fouling during ultrafiltration. *Journal of Dairy Science*, 1975, vol. 58, no. 10, pp. 1423–1432.
10. Antipov S.T., Titov S.A., Lavrenov A.L., and Soldatenko S.A. Prosvechivayushchaya elektronnaya mikroskopiya polyarizatsionnykh sloev, obrazuyushchikhsya pri ul"trafil"tratsii molochnoy syvorotki [Transmitting electron microscopy of polarization layers formed during ultrafiltration of milk whey]. *Khranenie i pererabotka selkhozsyria* [Storage and processing of farm products], 2009, no. 4, pp. 23–25.
11. Marcus C.R., B. Olivier, and de Haan Edward HF. Whey protein rich in α-lactalbumin increases the ratio of plasma tryptophan to the sum of the other large neutral amino acids and improves cognitive performance in stress-vulnerable subjects. *The American Journal of Clinical Nutrition*, 2002, vol. 75, no. 6, pp. 1051–1056.
12. Permyakov E.A. and Berliner L.J. α-Lactalbumin: structure and function. *FEBS Lett*, 2000, vol. 473, no. 3, pp. 269–274. DOI: 10.1016/S0014-5793(00)01546-5.
13. Beattie D. *Using RO/CEDI to Meet USP 24 on Chloraminated Feed Water Ultrapure Water Expo 2001 Technical Program*. Philadelphia, PA, April 2–4, 2001, p. 216.
14. Evdokimov I.A., Volodin D.N., and Dykalo N.Ya. Elektrodializ - perspektivnyy metod pererabotki molochnoy syvorotki [Electrodialysis is a promising method for processing whey]. *Pererabotka moloka* [Milk Processing[, 2001, no. 2, pp. 5–7.
15. Gorlov I.F., Khramtsov A.G., Titov S.A., et al. High tech of controlled pumping into whole muscle meat food. *Modern Applied Science*, 2015, vol. 9, no. 10, pp. 27–33. DOI: 10.5539/mas.v9n10p27.
16. Hiddink I., de Boer R., and Nooy P.F.C. Effect of various pretreatment on the ultrafiltration of sweet cheese whey at about 55°C. *Milchwissenschaft*, 1981, vol. 36 , pp. 657–663.
17. Mulder M. *Basic principles of membrane technology*. Dordrecht: Kluwer academic publishers, 1995. 510 p.
18. Ye A. and Singh H. Influence of calcium chloride addition on the properties of emulsions stabilized by whey protein concentrate. *Food Hydrocolloids*, 2000, vol. 14, no. 4, pp. 337–346. DOI: 10.1016/S0268-005X(00)00010-2.
19. Dickinson E. and Krishna S. Aggregation in a concentrated model protein system: a mesoscopic simulation of β-casein self-assembly. *Food Hydrocolloids*, 2001, vol. 15, no. 2, pp. 107–115. DOI: 10.1016/S0268-005X(00)00057-6.
20. Boulet M., Britten M., and Lamarche F. Aggregation of some food proteins in aqueous dispersions: effects of concentration, pH and ionic strength. *Food Hydrocolloids*, 2000, vol. 14, no. 2, pp. 135–144. DOI: 10.1016/S0268-005X(99)00059-4.
21. Arunkumar A., and Etzel Mark R. Negatively charged tangential flow ultrafiltration membranes for whey protein concentration. *Journal of Membrane Science*, 2015, vol. 475, pp. 340–348. DOI: 10.1016/j.memsci.2014.10.049.
22. Seely S. Is calcium excess in Western diet a major cause of arterial disease. *International Journal of cardiology*, 1991, vol. 33, pp. 191–198.

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