

Elaboration of the Process of Debarination – Defluorination of Molecular and Ionic Systems by Creation of Nanotechnologies and Nanosystems

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Abstract – In the work the problems of ionic and molecular selection of the solutions of various mineralization are considered. Along this line the nanotechnology of membrane two - stage ultra –and nanofiltration processes for debarination-defluorination of natural mineral water has been elaborated. The filtration process was carried out at membrane laboratory plant created for debarination-defluorination of Borjomi mineral water (Georgian resort “Borjomi”). Nanofiltration NFX, NFS (Synder Filtration) type membranes with were used. The quantitative index of the ions was determined by means of ion-selective membrane electrodes.

As a result of the research it was found that at various mass and concentration of ions of the waters of varying mineralization, because of the provision of the membranes of different ability for selection and of their optimal regime parameters the prediction of the control of quantitative index of the selection process of chemical elements has been made possible.

It has been established that the regulation of molecular and ionic composition of Borjomi natural mineral water is possible by means of baromembrane processes, confirmed by the methods of ionometric research, by the purposeful deionization of the mineral water. After filtration the concentration of barium and fluorine in the mineral water is reduced to maximum permissible concentration, in accordance with the regulation of Euro Union “Normative foundation of mineral waters”, 2003/40 EU, 2003.16.05

Keywords – Ionic Selection, Nanofiltration, Membrane Electrodes, Concentration, Mineral Water.

I. INTRODUCTION

Because of worsening of ecological problems in a number of the regions of the world the deficit of pure fresh and mineral waters is created. Therefore, the demand for treatment of mentioned waters by membrane technologies is increased. Baromembrane processes are widely used for purification-sterilization of the waters. Within recent years at the use of the membranes of high selectivity and conductivity the research of maximum possibilities of membrane nanotechnologies became topical. Purification of mineral waters, their sterilization, reduction of chemical components to maximum permissible concentration is of significant importance for the human health. The purification of the water from suspended particles and microorganisms is

necessary and, hereafter, partial defluorination-debarination in mineral water. So that the content of fluorine and barium must found in the range of permissible standard established by “Euro Union directive from 16.05.2003. 2003/40/EU “[1].

The problems of membrane filtration, ionic and molecular selection and debarination- defluorination are considered in the works of various authors.

In the work – “Ion-selective electrodes (ISE)” are considered which respond to the ions existing in the solution and are characterized by various degree of selectivity for concrete ions [2].

M.B.Rajkovic’ – The concentration of fluorine ions in the bottled mineral waters was determined by potentiometric

method, also it was mentioned that at small concentration (10^{-6} mole/dm³) of fluorine its determination is possible by the use of ion-selective electrode. The method is simple, reliable and cheap [3].

Amina Ramdani – Attention is drawn to the advantage of water purification by nanofiltration method. It was noted that the method is characterized by low power consumption, good selectivity and high productivity. The goal of their investigation involves the reduction of the concentration of fluorine-ions by the use of nanofiltration and disinfection [4].

Slawomir Gardos', Dorota Swiecicka – Research goal involved the determination of barium content in natural mineral and spring waters (gaseous, nongaseous and medium gaseous waters) which are bottled at the territory of Poland and estimation of the effect of above-mentioned metal on human health. The research was carried out by inductively coupled plasma optical emission spectrometry. The barium concentration in natural salt-containing and spring waters was determined in the range from 0.0136 mg/L to 1.12 mg/L and in the case of mineral water concentration of Ba²⁺ comprised 1.12mg/L, which exceeds MAC for mentioned metal [5].

Saince intensive and energy saving membrane nanotechnology, elaborated for simultaneous sterilization and debarination- defluorination of Borjomi natural mineral water, provides the compliance of filtrated mineral water with European standards. The treatment of the solution is carried out at temperature of 20°C and there is no need in thermal treatment at which the solution is damaged. Borjomi mineral water for drinking function may be widely used in medicinal – sanitary purposes. Ion-selective method of ion determination is characterized by precision, high sensitivity in regard to inorganic compounds. It is suitable and easy current method the little time is required for the analysis [6].

Research goal involves: the elaboration of the membrane nanotechnology for ionic and molecular selection of the liquid, experimental and theoretical research of the process of ionic selection for the solutions of various chemical composition; the elaboration of membrane two-step ultra- and nanofiltration universal nanotechnology for debarination-defluorination of the mineral water; the use of the method of ionometric analysis for determination of the amount of the ions in the water and, respectively, definition of anions and cations in the water by means of membrane ion-selective electrodes [7].

At debarination-defluorination of Borjomi mineral water the ultrafiltration al process for the water preliminary

treatment was used and nanofiltration one - for ionic selection in mineral water. The process was carried out at baromembrane laboratory plant by means of NFX, NFS – membranes. The ions in the water were determined at the device - ionometer – И-160.1МП and corresponding calibration and buffer solutions were prepared for the analysis of chemical elements. Ionometry, as one of the methods for the quality degree for natural waters and sewage, is introduced successfully in analytical practice and is based on the use of ion-selective electrodes which present the electrochemical semi-conducting element. Analytical methods, based on the use of the ion-selective electrodes, allow the direct determination of cations as well as of anions. Nanofiltration membranes, mastered at the end of the last century, perform successfully the separation of monovalent ions. Among the nanomaterials the porous membranes occupy a highly important place. This is determined by the following main reasons: the membranes themselves present the typical nanostructures which are two-dimensional binders or separate nanopores in the matrix polymeric or inorganic frame. The thin selective layers, in which the nanopores are mainly functioning, frequently, themselves, represent the nanolayer of the thickness up to 100 nm [8].

The functional properties of the membranes are, as usual, characterized by the size (R) of retained particles (reverse osmosis - $R < 3$ nm, which hold the hydrated iones or solved molecules; nanofiltrational – $3 \text{ nm} < R < 10 \text{ nm}$; ultrafiltrational – $0,01 \text{ m}\mu < R < 0,1 \text{ m}\mu$; microfiltrational - $0,1 \text{ m}\mu < R < 1 \text{ m}\mu$). Therefore, the technological processes, using the above – mentioned membranes, concern to the nanotechnologies.

As to mineral waters, among them the Borjomi water with unique complex of the minerals of volcanic origin may be marked out which act as “internal shower” and which cleans the organism perfectly well. It increases the immunity and is efficient at prophylaxis and therapy of the diseases caused by the disorder of the digestion and metabolism. Borjomi mineral water under study is slightly thermal and hydrocarbonate water, crops out in the surface in warm type, by the temperature of 38-41°C. The content of chemical compounds in it is sufficiently different. There are no toxic microelements, hydrogen sulfide from non-dissociated molecules. Arsenic, nitrates, nitrites and strontium exist in small quantities. In analysed mineral water the value, more than maximum permissible concentration, only have fluorine and barium. In accordance with Euro Union directive 2003/40 EU, 16.05.2003, barium musn't exceed 1mg/L and fluorine – 5 mg/L [1].

Various ions in varying mineral waters were studied in accordance with the mass and concentration, for treating of which membranes of NFX, NFS type were used. The methods of ionic selection were elaborated in relation to the composition of the solutions.

The chemical composition of various boreholes of Borjomi natural mineral waters was determined, as a result of the filtration the content of Barium and Fluorine had been brought to maximum permissible concentration on retention of appropriate amounts of other chemical components [9], [10].

The conditions were revealed empirically which determine the reduction of chemical elements in mineral water to maximum permissible concentration and to retain other chemical components in the limits of corresponding quantitative indices. For ionic selection the choice of optimal regime parameters for baromembrane process was carried out experimentally. As a result of experimental works the prediction of regulation of quantitative index of concentration of the selection of chemical elements in the solutions became possible [11].

In the course of the experiment it was taken into account that by increase of the temperature of separatory liquid the viscosity is reduced, diffusion coefficient of disperse phase is enhanced and concentration polarization is decreased.

II. EXPERIMENTAL PART

2. 1 Materials

In the course of the experiment were used: the untreated mineral water initial value and nanofiltrational membranes of NFX, NFS type with the atomic indices of which are NFX (150-300 DA), NFS (100-250 DA) (Synder Filtration).

Distilled water, the electric conductivity of comprises 5.02×10^{-4} cm/m. Sodium fluoride (NaF), potassium chloride (KCl) –Ukraine, barium chloride (BaCl_2), sodium chloride (NaCl), calcium chloride (CaCl_2), potassium nitrate (KNO_3), sodium hydroxide (NaOH) – Russia, glacial acetic acid (CH_3COOH), sodium acetate (CH_3COONa) sodium citrate - Czech Republic, were purchased in Tbilisi Joint – tock Company “Samaia.

2. 2. Methods

The experiment was carried out by the use of the membranes of NFX, NFS type. In the course of nanofiltrational process, by realization of laminary and turbulent regimes, the quantitative index of the ions was

determined ionometrically at the device - И-160. 1МП (Belarus)

2.2.1 Procedure of ionometric determination of Fluorine

The main standard solution of 0.1M NaF, containing 1900mg/L of F^- ions, and working standard solution were prepared by gradual 10-fold dilution of main standard solution to: 10^{-2} mole/L - 190mg/L of F^- ; 10^{-3} mole/L - 19.00 mg/L of F^- ; 10^{-4} mole/L - 1.90mg/L of F^- ; 10^{-5} mole/L- 0.190mg/L of F^- ;

Buffer solution for analysis was prepared by mixing of 58,5 g of NaCl, 15.0 g of glacial acetic acid (CH_3COOH), 102,2 g of sodium acetate (CH_3COONa), 3g of H_2O and 0,26 g of sodium citrate. For determination 10 ml of buffer solution was added to 50 ml of each analysed solution [12].

2.2.2 Procedure of ionometric determination of Barium

The main standard solution of 0.1M BaCl_2 , containing 1.42 mg/L of Ba^{2+} ions was prepared. Working standard solutions were prepared by gradual 10-fold dilution of main standard solution – 10^{-2} mole/L in which the concentration of Barium ions was equal – 2.17 mg/L; 10^{-3} mole/L – 3.06 mg/L; 10^{-4} mole/L – 3.06 mg/L [13].

2.2.3 Procedure of ionometric determination of Calcium

The main standard solution of 0.1 M CaCl_2 was prepared, containing 40008 mg/L of ions, working standard solutions were prepared by gradual 10-fold dilution of main standard solution - 10^{-2} mole/L, the concentration of Calcium ions comprises – 400.8 mg/L; 10^{-3} mole/L – 40.8 mg/L; 10^{-4} mole/L – 4.008 mg/L.

The KCl solution of 1 mole/L concentration was used as buffer solution for analysis, 10 ml of buffer solution was added to 50 ml of each analysed solution [14].

2.2.4 Procedure of ionometric determination of Chlorine

The main standard solution of 0.1 M KCl was prepared containing 3545 mg/L of Cl^- ions. Working standard solutions were prepared by gradual 10 – fold dilution of main standard solution - 10^{-2} mole/L, Chlorine concentration comprises – 345.5 mg/L; 10^{-3} mole/L – 35.45 mg/L; 10^{-4} mole/L – 3.545 mg/L. 1 mole/L solution of potassium nitrate was used as buffer solution for analysis. 10 ml of buffer solution was added to 50 ml of each analysed water [15].

2.2.5 Saturated solution of reference electrode

Saturated solution of KCl was prepared. 160 g of KCl was weighed. KCl was solved in the distilled water. It was transferred into the measuring flask of 500 ml volume, was

filled by the distilled water to the notch, then was placed on the cooker, was brought to boiling and was boiled over 5-10 minutes for CO₂ separation, then was cooled to 20°C and the reference electrode was filled by saturated solution of KCl, prepared by such manner [16].

2. 3. Monitoring of the research of nanofiltration process

Monitoring of nanofiltration process was carried out at the device ionometer - И-160.1МП (Belarus) taking into account minimal and maximum indices of determined ions (Fluorine, Barium, Calcium, Chlorine).

Fluorine was measured in the range from 0.5 mg/L to 10 mg/L, Barium – in the range from 0.2 mg/L to 3 mg/L, Calcium – from 20 mg/L to 150 mg/L and Chlorine in the range from 250 mg/L to 500 mg/L [12], [13], [14], [15].

In the course of nanofiltration process in the pressure chamber the laminary motion of the liquid is carried out in the conditions of chamber smooth walls and turbulent motion-at chamber toothed rack walls.

2. 4. Optimization and determination of regime parameters of nanofiltration process.

In the course of the experiment the amount of filtrate and concentrate was measured in the same range of the time in the conditions of corresponding temperature and pressure.

On the basis of experimental investigation, the indices of productivity and pressure were adjusted for selected pump for laminary and turbulent regimes. The value of circulation stream of membrane plant was determined in the conditions of preliminary defined temperature and pressure for laminary and turbulent streams.

Filtration degree obtained at the regimes of liquid laminary and turbulent motion was determined by ionometric method on the device ionomer -И-160.1МП (Belarus).

On the basis of the results, obtained by ionometric method the filtration degree is considerably increased in the identical technological conditions and various regimes of liquid stream (laminary, turbulent).

2. 5. Preliminary preparation of the samples of Borjomi mineral water

Experimental research of the process of preliminary treatment of Borjomi mineral water was planned on the basis of membrane technology of tangential filtration which is based on surface sieve effect. at which retardation of the particles is carried out only on the membrane surface. In this

case the treated liquid is fed to the membrane in tangential direction instead of perpendicular one.

At the first stage all samples of Borjomi mineral water were filtered on ultrafiltrational membrane with pore size of 0.5 μ m. Filtration degree was checked on turbidity measurer Turb - 555 IR (Germany). Turbidity of filtrated samples comprised 0.06 FNU units.

2.6. Preparation of defluorinated – debarinated samples of Borjomi mineral water

For nanofiltration of Borjomi mineral water the laboratory membrane universal plant: Danish DDS ultrafiltration, nanofiltration, reverse osmosis system Moodle LAB – 0.72; Serial № 7602192 of DDS Firm (Fig.1) was used.

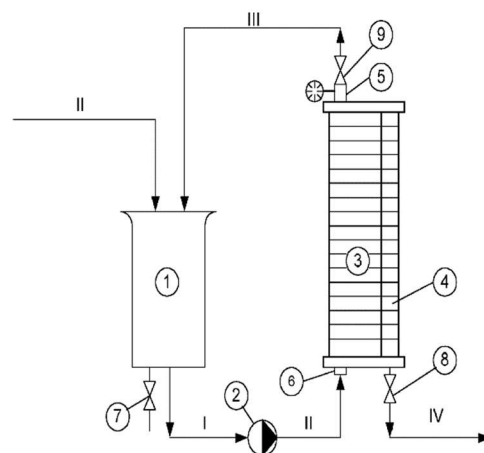


Figure 1 Principal scheme of nanofiltration experimental plant:

(1) Initial basin, (2) pump, (3) membrane apparatus, (4) Filtrate collector, (5) Back valve, (6) Pipe Connection, (7,8,9) Vales, I, II, III, IV - pipelines

In the samples treated by the polymer membranes of NFX, NFS type and in untreated ones Fluorine, Barium, Calcium and Chlorine were determined on ionometer И-160.1МП.

III. RESULTS AND DISCUSSION

3.1 Characterization of the process of the research of debarination and defluorination of Borjomi mineral water

By its composition Borjomi mineral water contains the rather large range of the chemical components. The quantitative indices of the components and chemical composition are distinct for any boreholes of Borjomi mineral water. The process of debarination and defluorination of Borjomi mineral water was studied and elaborated for the

waters of Likani, 37,25,42 and for the boreholes of the central park.

Determination of quantitative values of the ions of barium, calcium, fluorine and chlorine in Borjomi mineral water was carried out by ionometric method, by liquid filtration in the conditions of laminary and turbulent regimes for NFX, NFS – membranes and by the use of corresponding regime parameters. The initial value of the water was also determined in the untreated sample.

According with the directive of Euro Union (2003 year) in mineral water Barium mustn't exceed 1 mg/L and Fluorine – 5 mg/L. Permissible amount range of Calcium is from 20 mg/L to 150 mg/L and for Chlorine – from 260 mg/L to 380 mg/L [1].

Borjomi natural mineral water from above – mentioned boreholes was treated in two stages. At the first stage, till nanofiltration, the turbidity index was determined (Table 1) on the device - Turb 555IR. Mineral water was passed on the ultrafiltrational membrane with the pores of 0.05 μm . As result, the initial turbidity of mineral water, in accordance with the formazin unit, is reduced from 1.09 – 6.33 FNU to 0.06 FNU in accordance with the boreholes (Figure 2).

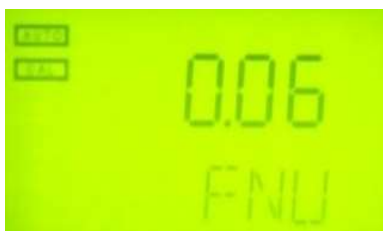


Figure 2. Treated water of the borehole 37

Table 1 Turbidity index of Borjomi untreated water in accordance with the boreholes

Name of boreholes	Turbidity index FNU
Borehole 37	2,05
Borehole 41	1,09
Borehole 25	2,03
Borehole „Likani“	6,33
Borehole “ Central park” water	1,37

Quantitative indices of the ions: barium, fluorine, calcium, chlorine were determined in the filtrate, obtained from nanofiltration and in initial untreated sample.

In the water of borehole 37 the initial amount of barium comprises 3.27mg/L and of fluorine – 5.26mg/L, which exceeds the permissible concentration. Along with it, the quantitative index of calcium is equal to 51.7 mg/L and of chlorine – 386 mg/L.

By the use of NFX – membran in the conditions of laminary regime barium amount decreased to 1.60 mg/L and of fluorine –to 3.82 mg/L.

By the use of NFS – membran barium amount reduced to 1.05 mg/L and of fluorine –to 4.11 mg/L.

Along with it, for calcium and chlorine the component quantitatively permissible values are retained, in particular 28.2 mg/L for calcium and 348 mg/L for chlorine (Table 2, Figure 3)



Figure 3. Quantitative indices of chemical components of initial and treated Borjomi mineral water in the condition of laminary regime of borehole – 37.

In the conditions of turbulent regime and by the use of NFX- membran and technologies the Barium amount is reduced to 1.23 mg/L and Fluorine one – to 3.58 mg/L.

By the use of NFS- membran and technologies Barium amount is decreased to 0.958 mg/L and Fluorine one to 3.84 mg/L.

Along with it, the quantitative permissible values for the components are retained for Calcium and Chlorine: in particular, for Calcium – 25.5 mg/L and for Chlorine – 340 mg/L (Table 3, Figure 4).



Figure 4. Quantitative indices of chemical components of initial and treated Borjomi mineral water in the conditions of turbulent regime of borehole 37

The boreholes 41,25, “Likani” and “Central park” were treated by identical manner.

laminary as well as of turbulent regimes are presented in Tables 2 and 3.

Quantitative indices of chemical compounds of Borjomi mineral water in the conditions of

Table 2 Quantitative indices of chemical components of initial and treated Borjomi mineral water in the conditions of laminary regime

Borehole	Technology	Ba, mg/L	F , mg/L	Ca, mg/L	Cl, mg/L
37	Untreated	3.27	5.26	51.7	386.0
37	NFX	1.60	3.82	28.2	348.0
37	NFS	1.05	4.11	38.5	359.0
41	Untreated	3.46	6.96	97.2	352.0
41	NFX	1.09	4.82	74.2	292.0
41	NFS	0.937	6.52	15.8	349.0
41	2NFS	1.26	-	-	334.0
25	Untreated	3.58	9.67	46.8	372.0
25	NFX	1.11	5.10	32.5	328.0
25	NFS	1.64	6.48	30.8	335.0
Likani	Untreated	2.34	4.06	127.0	243.0
Likani	NFX	0.738	2.26	56.8	206.0
Likani	NFS	0.833	2.95	104	199.0
Central park	Untreated	3.11	5.76	97.9	323.0
Central park	NFX	0.875	3.91	71.8	289.0

Central park	NFS	1.16	4.69	51.6	291.0
Permissible range		<1	<5	20 - 150	260 - 380

Table 3 Quantitative indices of chemical components of initial and treated Borjomi mineral water in the condition of turbulent regime

Borehole	Technology	Ba, mg/L	F, mg/L	Ca, mg/L	Cl, mg/L
37	Untreated	3.27	5.26	51.7	386.0
37	NFX	1.23	3.58	25.5	340.0
37	NFS	0.958	3.84	38.5	347.0
41	Untreated	3.46	6.96	97.2	352.0
41	NFX	0.854	4.28	69.5	273.0
41	NFS	0.614	5.84	12.0	318.0
41	2NFS	1.26	-	-	334.0
25	Untreated	3.58	9.67	46.8	372.0
25	NFX	0.973	4.57	29.2	305.0
25	NFS	1.23	5.77	24.2	328.0
Likani	Untreated	2.34	4.06	127.0	243.0
Likani	NFX	0.641	1.83	48.6	199.0
Likani	NFS	0.780	2.72	97.6	194.0
Central park	Untreated	3.11	5.76	97.9	323.0
Central park	NFX	0.623	3.53	68.4	266.0
Central park	NFS	0.996	4.50	49.1	285.0
Permissible range		<1	<5	20 - 150	260 - 380

IV. CONCLUSION

- By empirical approach the conditions were revealed which provide the reduction of chemical elements in mineral water to maximum permissible concentration and retention of other chemical components in the range of necessary quantitative index.

-In response to the research it was established that at various mass and concentration of the ions in the waters of varying mineralization, as a result of provision of the membranes of different ability and of optimal regime parameters for them, the prediction of regulation of quantitative indices of concentration in the selection process for chemical compounds in the solutions has been made possible.

- It was established that the regulation of molecular and ionic composition of Borjomi natural mineral water is possible by the use of baromembrane processes which is confirmed by the methods of ionometric research by purposeful deionization of the mineral water.

- At the treatment of Borjomi mineral water the simultaneous removal of all external mechanical inclusions, undesirable impurities and microorganisms takes place, providing obtaining of high-quality, crystallinely transparent, sterile and eco-safe production without sediment.

-We think that the separation of fluorine concentrate, formed at the treatment of mineral water and its secondary use is possible; obtained concentrate may be treated by nanofiltration for significant increase of fluorine amount in it. The our experiments on Borjomi mineral water revealed this possibility.

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