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The concept of multivariant use of geothermal water concentrates

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ABSTRACT

Geothermal waters usually contain elevated concentrations of specific elements, which could be valuable for reuse. The hydrogeochemical composition of recovered concentrates strictly determines potential management and reuse for other purposes, including balneology sector. Natural water, which possesses curative parameters, can be concentrated by use membrane processes to produce curative solutions or crystalline salts used for healing baths or inhalations. Concentrates can be a valuable resource for production of mineral salts, metals, valuable chemicals, and also magnesium, calcium, potassium, and sodium salts or other products for cosmetology and balneology industry. The aim of this work was to present the results of the assay oriented toward examination of the potential further multivariant use of concentrates gained in two-stages of NF-RO (nanofiltration–reverse osmosis) treatment system of geothermal waters. The assessment of the possibility of domestic use of concentrates gained as a therapeutic product, for example, in health baths, required the assessment in order to meet the requirements of the local regulations. The study results revealed that concentrates gained from two-step NF-RO system, due to the concentration of the desired ingredients, were a potential source of different valuable mineral solutions, because of high content of sodium, magnesium, chlorides, silica, and other components used for therapeutic purposes.

Keywords: Concentrate; Desalination; Geothermal water; Reverse osmosis; Balneology

1. Introduction

Membrane processes, in particular reverse osmosis (RO) and nanofiltration (NF), are widely applied in water desalination, the production of potable water, and, recently, also in tertiary wastewater treatment [1,2]. The technology faces number of challenges consequent on the ever-increasing efficiency demand in parallel with environment-friendly management of the produced brines, also called as concentrates or retentates, which are commonly regarded as waste streams [3,4]. RO process is currently one of the most used seawater, wastewater, or geothermal water desalination and treatment technology all over the globe [5]. Currently more than 50% of the operated desalination plants use membrane technology, mostly RO, because of its simplicity and reliability. A relatively low energy cost of RO compared with other processes, its continuous advancement caused by use of novel membrane materials, improved design, possibility of combining with other processes, and also optimization assays further reducing the specific energy consumption and the cost of desalinated water also play important role [2]. The desalination systems may be used to separate dissolved solutes, including single charged ions (such as Na^+, Cl^-) from feed geothermal water via selected membrane [6]. However, it is assumed that RO process cannot be used for desalination

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of high saline concentration effluents, which contain more than 65 g of salts/L, because of considerably osmotic pressure increase along with the salt concentration leads to a significant increase in energy use [7]. Observed in recent years the increase in geothermal waters use, mainly for heating and recreation purposes, has led the researchers to carry out assays, the aim of which is to develop new technologies and methods enabling comprehensive and multivariate management of waste, chilled geothermal waters. These waters, due to their physicochemical composition, are often additionally therapeutic waters, as potentially they are a source of many valuable and useful ingredients. The use of membrane processes for their treatment, mainly to obtain potable water, also generates a by-product – a concentrate, which due to the increased content of separated particles, dissolved salts, and other substances (in many cases almost double in concentration than the raw geothermal water), can potentially be further used, e.g., for balneological purposes [8,9]. The gained concentrate may be a source of inorganic and organic compounds that can be recovered using appropriate methods and procedures. Moreover, the physicochemical parameters, the amount and, consequently, the management and potential reuse of obtained concentrates will depend primarily on the quality of the desalinated water, the quality of the obtained permeate, the recovery rate (mostly from 35% to 85%), process parameters, the possible use of chemicals (e.g., addition of an antiscalant), cleaning procedures, and the recovery method used [10–14]. Brines can potentially be utilized by the recovery and the production of chemical substances (e.g., boric acid), metals or ions and substances useful for the cosmetics or balneology industry [12]. Kin et al. [15] presented that in the case of inland installations, the aspect of the amount, quality, and management of high-salinity concentrate was particularly important, due to the location of desalination plant away from the sea or the ocean. The effective management of the high salinity concentrate is an important economic factor of the investment. The improper concentrate management can result in adverse environmental effect related to high salinity and concentration of metals and other emerging dissolved solutes [16,17]. The physicochemical parameters of feed geothermal water will determine a possible reuse of a concentrate for balneological purposes or a recovery of selected elements. The therapeutic value of geothermal waters is determined by their temperature, variety of dissolved ions, gases, and trace elements. In many countries, there are specific law regulations and rules used for the classification of surface and groundwaters [18–20]. In Poland, if groundwater is not contaminated, but characterizes with natural variations in physical and chemical parameters, contains at least one specific component (pharmacodynamic factors), and/or has a temperature above 20°C, it is then considered as a therapeutic water [21]. Such a water usually contains the combination of main cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+), anions (HCO_3^-, Cl^-, and SO_4^{2-}), and specific compounds (which can determine the medicinal value of water) in varying amounts. These dissolved components bring out various therapeutic benefits of thermal bathing [2]. Gryta [22] showed that natural water, which possessed curative parameters, could be concentrated by use of membrane processes to produce curative solutions or crystalline salts used for healing baths or inhalations. Concentrates from geothermal water treatment can be a valuable resource of mineral salts [23,24], metals [25] (e.g., lithium [26,27] and strontium [28]), chemicals (e.g., boric acid, magnesium oxide [29] or magnesium and calcium, potassium, and sodium salts [30]) or products for cosmetology and balneology industries [30]. Tang et al. [31] showed possible high-selective separation of divalent ions from RO retentate. After application of membrane processes, nearly all of the compounds present in the feed water (mostly NaCl) are found in the concentrate. NaCl is an important material widely used in soda and chlor-alkali industry. The reuse of high salt resources present in membranes' retentate is a perspective technology and it is the subject of many scientific researches [30,32–34]. Kim [11] reviewed possible salt recovery techniques and showed their economic analysis. Additionally, the separation of antiscalants from RO brine has been found to be very important, when salt production is to be performed [35]. Moreover, the concentration of heavy metals in desalination concentrates may exceed discharge limits and it can limit possible reuse of brine, because of their negative influence on the environment [36]. Xiu et al. [37] and Xu et al. [38] discussed different technologies used for selective removal of arsenic and monovalent ions from RO concentrate.

The aim of this work was to present the results of the assay focused on the examination of the further potential multivariant use of concentrates gained in two-stage NF-RO treatment system of geothermal waters. The possibility of using gained concentrates as a therapeutic products, for example, in health baths, required assessment in order to meet the requirements of the Regulation of the Minister of Health from 13th April 2006 on the scope of research necessary to determine the curative properties of natural medicinal raw materials and the curative properties of climate, criteria for their assessment and the template of the certificate confirming these properties [39].

2. Methodology and materials

2.1. Membranes and apparatus characteristic

The tests were conducted with the use of two-step desalination NF-RO system using the American Osmonics Inc. company's, Minnetonka, USA, SEPA CF-HP type membrane module, in the high-pressure version operated in the cross-flow mode with the use of NF270, NF90, and ROBW30FR-400 DOW FILMTEC™ membranes and two geothermal waters from Poland area. The geothermal water was placed in the raw water tank, from which feed stream was pumped directly to the membrane cell and consequently, to the membrane. Water flowed tangentially across the membrane surface. The flow was fully controlled and could be laminar or turbulent. It depended on the basic parameters and glow velocity used. The membrane was placed in membrane cell and its active area amounted 155 cm^2. Membrane process divided inflowing stream into two separate ones: (1) a permeate – a part of the feed water, which permeated through the membrane surface, flew out through permeate outlet and was collected in a vessel and (2) a concentrate – a part of the feed water, which did not flow through the membrane, which contained rejected dissolved compounds, and was continuously recycled into the feed tank.

The first step of two-stage NF-RO treatment system was the NF process of raw geothermal waters with the use of either NF270 or NF90 membrane and the second step was the

RO process. The permeate obtained in NF process was used as the feed water for the second stage of the treatment system. Both processes, NF and RO, were conducted until 50% recovery of feed water (50% of permeate and 50% of concentrate in relation to raw water volume) was obtained. The NF process was carried out at the transmembrane pressure of 10 bar, while the RO process was conducted at the pressure of 15 bar. Due to the precisely intended use of obtained permeates and concentrates, the tests proceeded without addition of any chemicals. During all tests, almost constant temperature of feed waters was maintained by heat exchanger placed in the raw water tank. The scheme of the apparatus applied in both NF and RO processes is presented in Fig. 1.

Three DOW FILMTEC™ membranes were chosen for the tests, including two NF and one RO membranes commercially marked as: NF270, NF90, and ROBW30FR-400. The membranes characteristic is shown in Table 1.

All membranes were conditioned right before tests by means of filtration of deionized water.

2.2. Geothermal waters parameters

Two geothermal waters from Poland area were involved in the studies and thus analyzed according to selected physicochemical parameters. The first geothermal water (TW-1) characterized with elevated mineralization (about 2.5 g/L), silica content (61 mgSiO_2/L), and also relatively high concentrations of calcium (194 mg/L), magnesium (41 mg/L), boron (9.8 mg/L), and other micro and macronutrients. TW-1 was of SO_4-Cl-Na-Ca hydrogeochemical type, according to the Szczukariew–Priklonski classification. The second geothermal water (TW-2) had evidently higher mineralization (6.7 g/L, almost three times higher than TW-1), lower concentration of silica (26 mgSiO_2/L), calcium (127 mg/L), magnesium (21 mg/L), and boron (0.95 mg/L) and it was of Cl-Na hydro-geochemical type. In all tests, the temperature of both TW-1 and TW-2 was 23°C. The electrical conductivity (EC), pH, and temperature value of raw geothermal waters, permeates, and concentrates were measured directly after process in the laboratory using

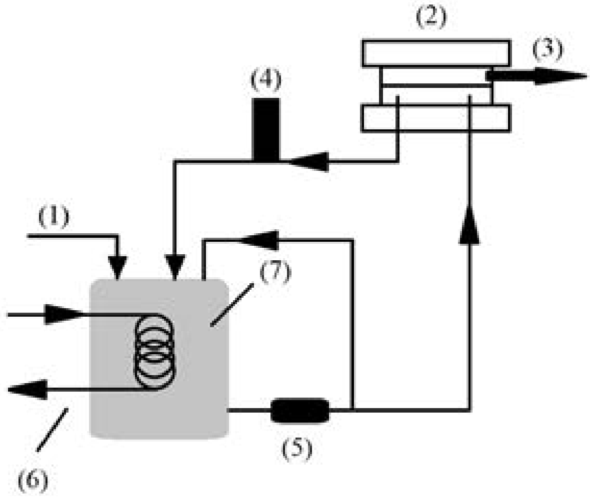

Fig. 1. The scheme of apparatus applied in both nanofiltration and reverse osmosis processes ((1) raw water inlet; (2) membrane cell; (3) permeate outlet; (4) rotameter; (5) pump; (6) heat exchanger; (7) raw water tank).

the electrometric method. The detailed chemical and physical characteristics of raw geothermal waters, permeates, and concentrates were determined in the accredited laboratory of Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology in Krakow using inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), and titration method (for chloride ions, in accordance with accredited testing procedures).

3. Results and discussion

3.1. The results of geothermal waters treatment

The specific chemical and physical composition of raw geothermal waters, permeates, and concentrates after both NF and RO processes are shown in Table 2. In reference

Table 1
Membranes characteristic [40–42]

	NF270	NF90	BW30FR-400
Material	Polyamide thin-film composite	Polyamide thin-film composite	Polyamide thin-film composite
Maximum operating temperature (°C)	45	45	45
pH operating range	2–11	2–11	1–13
Maximum operating pressure (MPa)	4.1	4.1	4.1
Retention coefficient	>98% $MgSO_4$ 50% NaCl	>98% $MgSO_4$ 90%–96% NaCl	99.65% NaCl
Application	Ideal for enabling medium to high salts passage and hardness passage from water where good organic removal is desired with partial softening	Provides high productivity performance while removing a high percentage of salts, nitrate, iron, and organic compounds	Designed to purify water with high biological and organic fouling potential in systems with well-controlled pretreatment; characterized as element which offers exceptional fouling resistance, cleanability, and long-term efficiency

Table 2
Physicochemical parameters of NF-RO system streams

Parameter	TW-1			TW-2					
	Raw water for NF270 (mg/L)	NF270 concentrate (mg/L)	RO concentrate (NF permeate as feed water) (mg/L)	Raw water for NF270 (mg/L)	NF270 concentrate (mg/L)	RO concentrate (NF270 permeate as feed water) (mg/L)	Raw water for NF90 (mg/L)	NF90 concentrate (mg/L)	RO concentrate (NF90 permeate as feed water) (mg/L)
Mineralization	2,587	3,151	1,610	6,697	7,432	6,508	6,029	11,073	1,233
TDS	2,416	2,969	1,489	6,560	7,264	6,392	5,891	10,825	1,255
H-G type[a]	SO_4-Cl-Na-Ca	SO_4-Cl-Na-Ca	Cl-Na	Cl-Na	Cl-Na	Cl-Na	Cl-Na	Cl-Na	Cl-Na
EC[b] (mS/cm)	3.35	3.77	2.57	10.04	10.91	9.86	10.39	17.67	2.37
pH	6.80	7.62	7.52	6.73	7.59	7.34	7.39	8.40	7.20
Na^+	488.68	552.75	394.95	2,417.00	2,664.00	2,374.00	2,061.06	3,854.90	478.16
K^+	47.64	54.93	38.51	20.45	23.61	19.60	18.39	35.03	6.56
Ca^{2+}	194.10	291.85	72.37	127.83	150.45	118.31	123.62	219.93	2.97
Mg^{2+}	41.58	62.62	13.24	21.54	24.89	18.62	21.08	38.63	0.65
Cl^-	487.90	430.20	689.90	3,719.00	4,053.00	3,679.00	3,407.00	6,220.00	708.40
SO_4^{2-}	854.71	1,276.59	16.29	72.34	132.27	22.27	70.45	133.92	3.00
HCO_3^-	343.30	364.00	241.60	273.80	335.00	231.90	275.00	496.70	44.60
H_2SiO_3	79.43	72.43	96.13	34.01	35.53	33.18	36.07	58.38	5.50
I^-	0.100	0.070	0.211	0.053	0.056	0.123	0.085	0.024	0.010
Li^{2+}	1.138	1.202	0.856	0.174	0.189	0.176	0.170	0.286	0.032
Fe^{2+}	0.232	0.117	0.071	0.489	0.121	0.022	0.480	0.035	0.037

[a] Hydro-geochemical (H-G) type according to the Szczukariew–Priklonski classification; [b]Electrical conductivity.

to the result of the research presented in Table 2, it can be noticed that the selected physicochemical parameters of concentrates gained from NF and RO processes for both waters, including main cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}), anions (HCO_3^-, Cl^-, and SO_4^{2-}), and specific compounds, which can determine the medicinal value of water (Table 3), appeared in varying amounts. The physicochemical parameters of feed geothermal water determined possible reuse of concentrates for balneological purposes or for the recovery of selected elements.

The raw waters TW-1 and raw TW-2 were hydrogeochemically classified as SO_4-Cl-Na-Ca and Cl-Na, respectively. The mineralization and total dissolved solid (TDS) of raw TW-2 was three times higher than for TW-1. Moreover, pH value of raw TW-1 was 6.80 and in NF concentrate it increased up to 7.62. For TW-2, with the use of NF270 and NF90 membrane, pH value increased from 6.73 to 7.59 and from 7.33 to 7.52, respectively. The change of electrical conductivity and pH value for processes with the use of NF270 membrane was similar for both tested waters. Each mineral water can be medicinal water, regardless of whether it contains specific components, presented in Table 3. Natural geothermal water marked as TW-1 characterized with elevated concentrations of main cations and anions. The results indicated that in the first stage of desalination using NF module, the amount of main ions significantly increased in concentrate. The only exception was observed for chlorides, for which the concentration decreased from almost 488 to 430 mg/L. In both cases related to TW-1 raw geothermal water and NF270 concentrate, the concentration of silica exceed the value of 70 mg H_2SiO_3/L, which was the pharmacodynamic factor. NF270 membrane used in TW-2 water treatment caused the lower retention of TDS, as well as of calcium and magnesium content, in reference to TW-1. The reason of less effective retention of selected parameters was the high TDS value of TW-2. To obtain higher concentrations of desired ions, more compact NF90 membrane was applied. The results presented in Table 2 indicated that for NF90 membrane concentration of most parameters significantly increased. The most visible changes were observed for main mono- and divalent ions. Both NF membranes caused significant increase of SO_4^{2-} in concentrate for TW-2 NF90 treatment. In order to assess possible concentrates reuse for therapeutic purposes, the concentration of metasilicic acid was evaluated. The high retention of the compound was identified for TW-2 with the use of NF90 membrane, however its value still did not exceeded 70 mg/L. For iodide and lithium ions the use of NF process caused slight decrease or increase in their concentration, depending on the membrane type used. The concentrations of iron ions decreased in all gained concentrates. The second stage of water desalination was applied to elevate the water recovery rate and to increase the concentration of valuable ions in concentrates. The permeates obtained from NF processes were introduced to RO module as feed waters. It was provided to increase process efficient, potential use of water permeates as drinking waters, and also to expand possible concentrates reuse in balneology or cosmetology industry.

The results of selected physicochemical parameters of concentrates gained from the RO processes are presented in Table 2. The experimental data showed that after the second stage of desalination for TW-2 water, a slight increase in concentration of chlorides (only after NF270 process) was observed. Whereas, for TW-1 RO concentrate relatively high values of chlorides concentration were obtained. However, for TW-2 concentrates, most of the selected parameters were significantly different and depended of feed water used. The use of second RO desalination stage allowed for additional recovery of desired ions from NF permeates. The rate of the recovery, that is, the concentration of the particular component, depended primarily on the efficiency of the first desalination stage. The more it was recovered by the NF process (mainly with NF90 membrane), the lower rates of concentrations of given components were obtained by the RO process. Despite the low concentrations of individual desirable ions obtained for RO concentrate (for the NF90 membrane), the overall effectiveness of the process remain high. The use of RO allowed for a greater recovery of lithium, iodine ions and also metasilicic acid from desalinated water. In reference to possible further reuse of concentrates gained for balneological purposes, high recoveries of most of the analyzed parameters were observed. For TW-1, the highest concentrations in RO concentrate were observed for chlorides, sodium, and bicarbonate ion. Moreover, the use of RO process enabled to increase the recovery of metasilicic acid and iodide ions. Similar tendency was observed for TW-2, in the process with the use of NF270 membrane, where application of RO process enabled to increase the recovery of iodide and lithium ions. Based on the results presented in Tables 2 and 3, it can be concluded that both raw waters and NF or RO concentrates

Table 3
Classification of therapeutic groundwaters based on their pharmacodynamic factors [43,44]

Total dissolved solids (TDS)	Pharmacodynamic factors – specific components		Temperature
≥1 g/L	2 mg F^-	Fluoride water	>20°C (thermal water)
	1 mg I^-	Iodide water	
	1 mg S(II)	Sulfide water	
	70 mg H_2SiO_3	Silica water	
<1 g/L	10 mg Fe(II)	Ferruginous water	<20°C (cold water)
	74 Bq	Radon or radioactive water	
	250 mg free CO_2	Carbonate water	
	1,000 mg free CO_2	CO_2-rich water, carbonated water	

can be regarded as a valuable resource for production of mineral solution, because of high content of sodium ions and chlorides. These waters can also potentially be a source of other products for cosmetology and balneology industries. After application of membrane processes, nearly all of the compounds in the feed water (mostly NaCl) are remained in the concentrate. Moreover, the relatively high mineralization and content of other main ions, metasilicic acid and lithium is observed in generated concentrates. The amount of heavy metals in desalination side streams may exceed discharge limits and thus it can limit possible reuse of brine, because of its negative influence on the environment.

3.2. The assessment of the possibility of the reuse of concentrates gained in membrane processes

The assessment of the possibility of using the concentrates regarded as a medicinal products, for example, in health baths, in Poland requires the assessment in order to meet the requirements of the Regulation of the Minister of Health [39]. The highest acceptable concentrations of undesirable and toxic components in therapeutic waters, in reference to their concentrations in both waters (and in dependence of membranes used) are shown in Table 4. A detailed comparison of the permissible content of toxic components in relation to the therapeutic waters used as the drinking water, inhalation and external use water revealed that in both TW-1 concentrates content of aluminum, chromium (only for RO concentrate) and boron exceeded permissible content and they could not be used in drinking water therapy and inhalations. The concentration of aluminum and chromium in RO concentrate exceeded permissible values about two times, while for NF concentrate only aluminum content slightly exceeded the established standard. The results of the tests conducted with the second geothermal water, with the use of NF270 membrane, revealed that both concentrates (NF and RO) could not be used in drinking water therapy and inhalations because of the elevated concentration of chromium. Its value exceeded the permissible level more than three times for both concentrates. In contrast, the results of the concentrates gained in the tests with the use of NF90 membrane indicated that both concentrates could potentially be used in drinking therapy or they could be a source of a number of valuable substances.

For many years, geothermal waters have additionally been used as a source of therapeutic salts and also as a source product for cosmetics production and balneology industry. For example, waters with therapeutic properties were detected in Blue Lagoon (silicate-rich waters), La Roche–Posay Thermal Center (selenium-rich waters) and in the Dead Sea region (due to high salinity, and also atmospheric, solar, chemical, and thermal properties) [45,46]. Concentrated geothermal water could potentially be reused for the same purposes.

4. Summary and conclusions

The aim of this work was to present the results of the study focused on the examination of the potential further multivariant reuse of concentrates gained in two-stage NF-RO treatment system applied for geothermal water desalination.

Table 4
Concentration of undesirable constituents in obtained concentrates, according to regulation of Minister of Health (MH) [39]

Parameter	The highest acceptable concentrations of undesirable components			TW-1			TW-2					
	Drinking treatments (mg/L)	Inhalations (mg/L)	External use (mg/L)	Raw water for NF270 (mg/L)	NF270 concentrate (mg/L)	RO concentrate (NF permeate as feed water) (mg/L)	Raw water for NF270 (mg/L)	NF270 concentrate (mg/L)	RO concentrate (NF270 permeate as feed water) (mg/L)	Raw water for NF90 (mg/L)	NF90 concentrate (mg/L)	RO concentrate (NF90 permeate as feed water) (mg/L)
Ni^{2+}	0.03	0.03	–	0.001	0.011	0.004	0.001	0.009	0.012	0.003	0.022	0.028
Pb^{2+}	0.01	0.01	–	0.0001	0.0001	0.0001	0.0001	0.0005	0.0001	0.0003	0.0006	0.0004
Hg^{2+}	0.001	0.001	–	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003	0.0006	0.0001
Cd^{2+}	0.003	0.003	–	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Al^{3+}	0.1	0.1	–	0.008	0.176	0.210	0.005	0.038	0.031	0.005	0.005	0.005
Cr^{3+}	0.01	0.01	–	0.019	0.006	0.011	0.043	0.038	0.036	0.037	0.008	0.005
B	5.00	30.00	–	9.76	7.64	9.92	0.95	1.01	0.94	1.03	1.04	1.08

The obtained results indicate that analyzed system can be a promising technology for treatment and concentration of geothermal waters in order to gain products for balneology and cosmetology purposes. As a result of the NF and RO processes carried out in the two-stage system, high-quality concentrates are obtained. For the second geothermal water analyzed, obtained concentrates characterize with the high content of desired compounds, especially high content of sodium, which amount to more than 2,000 mg/L for most process configurations. However, in the NF process with the use of the NF90 membrane, slightly more preferable concentrations of selected parameters are observed than in case of less compact NF270 membrane. Due to physicochemical parameters of the first geothermal water, after concentration processes, its concentrates possess elevated concentrations of ingredients beneficial for therapeutic purposes. Additionally, the assessment of the possibility of using the concentrates as a medicinal products in Poland, for example, in health baths, requires the assessment in order to meet the requirements of the Regulation of the Minister of Health. The results of the research show that in TW-1 concentrates, contents of aluminum, chromium (only for RO concentrate), and boron (NF and RO concentrate) exceed permissible level for drinking therapeutical treatment and inhalations. Generally, the research shows that two-step desalination of geothermal water can be used as an effective method to obtain concentrates that can be applied for external use, for example, balneological treatments, sanitary baths, and recreational pools and, in some specific cases in drinking therapy and inhalations. The concentrates gained from two-step NF-RO system, due to the high concentration of the desired ingredients, are a potential source of different minerals, because of the high content of sodium, magnesium, chlorides, silica, and other components used for therapeutic purposes. The research indicates that membrane processes can potentially be used as methods to obtain valuable products for therapeutic, balneology, or cosmetic purpose.

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