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DESALINATION OF SEAWATER. OSMOTIC PROCESS FOR "BLUE ENERGY" AND ESTIMATION FOR DESALINATION

Seawater, a vast resource, holds fresh water that is increasingly crucial in industrially developed countries. The demand for freshwater for domestic use, agriculture, and industry in these nations far surpasses the available supplies, leading to freshwater scarcity. Your invaluable work in water resource management and environmental science, which is pivotal in addressing this issue, is greatly appreciated. This issue is not limited to specific countries in places like Israel and Kuwait, where the level of precipitation is very low, and freshwater reserves do not meet the increasing needs due to the modernization of the economy and population growth. This global relevance underscores the importance of desalination technologies as a potential solution. As we explore the potential of desalination technologies, we are presented with a promising solution to water scarcity- the vast seas and oceans as alternative water sources. This potential is particularly significant in your field of research and expertise, underscoring the relevance of this paper to your work. The countries with the cleanest drinking water usually have large freshwater reserves in lakes, rivers, underground waters, and glaciers, providing a reassuring buffer against water scarcity. Brazil, for instance, benefits from abundant freshwater from the Amazon River and its extensive basin system. Canada boasts numerous lakes and river systems. The United States include large freshwater reserves in the Great Lakes, numerous rivers, and groundwater. Colombia has large freshwater resources, primarily due to numerous rivers and groundwater. Chile is rich in glacier water, further enhancing its water security. This diverse range of water resources underscores the need for desalination technologies to supplement these sources. In Europe, the Scandinavian countries Norway and Sweden have natural resources for clean drinking water from mountain rivers and lakes. Denmark is flat, but like the other Scandinavian countries, it maintains strict environmental policies and a high-quality water supply network. Germany has a well-developed water resource management system that ensures high-quality drinking water. German drinking water typically comes from underground sources, which are considered very clean, as well as from rivers and dams. There are many glacier sources and rivers in the Alpine countries of Austria, Switzerland, and Italy. Ukraine and Romania have large amounts of drinking water from the Carpathians. Bulgaria is rich in rivers and dams. It has 141 mountain peaks with heights of over 2000 m. Some countries have extensive natural resources that help them to provide the necessary drinking water for their citizens, although distribution and accessibility may depend on regional and economic conditions. The following countries have desalination technologies for clean drinking water from seawater – Saudi Arabia, United Arab Emirates, Israel, Singapore, Australia, Spain, and California (USA).

Keywords: desalination, reverse osmosis, chemical precipitation, distillation, ion exchange, electrodialysis, osmosis, "blue energy".

1. Introduction

Seawater desalination has been a reliable and economical water resource, since the second half of the 20th century. In the 21st century, integrating renewable energy sources with producing fresh water from seawater has led to the development of new technologies capable of minimizing the environmental impact of desalination processes due to their intense energy consumption [1].

Along with NaCl, seawater contains K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Br^-, F^-, H_3BO_3, which can be extracted from seawater on the industrial scale [2] (Table 1).

Lithium (Li), rubidium (Rb), phosphorus (P), iodine (I), iron (Fe), zinc (Zn), and molybdenum (Mo) are among the substances found in seawater at concentrations from 0.01 to 1 ppm. About 30 other elements are also found in seawater at lower concentrations [2].

The high concentration of salts makes seawater unsuitable for drinking and domestic purposes. Therefore, it must be desalinated and treated to reduce the salts to 1 g L^{-1}.

The research aims to show the method for seawater desalination and the parameters of the osmosis for desalination after the “blue energy” process.

The investigation aims to determine the percentage of seawater that can be desalinated without additional energy expenditure. The proposed method separates lake or river water from seawater with a semipermeable membrane. Subsequently, another desalinated method can be applied.

Table 1. **Average result of the chemical compounds and ions in seawater**

Chemical compounds and ions	Content, g kg^{-1}	Concentration, mol L^{-1}
Chlorides (Cl^-)	19.35	0.55
Magnesium (Mg^{2+})	1.29	0.054
Calcium (Ca^{2+})	0.412	0.010
Sodium (Na^+)	10.76	0.47
Potassium (K^+)	0.40	0.010
Sulfates (SO_4^{2-})	2.71	0.028
Carbon dioxide (CO_2)	0.106	2.3×10^{-3}
Bromides (Br^-)	0.067	8.3×10^{-4}
Boric acid (H_3BO_3)	0.027	4.3×10^{-4}
Strontium (Sr^{2+})	0.0079	9.1×10^{-5}
Fluorides (F^-)	0.001	7.0×10^{-5}

2. Methods

2.1. Standards for water quality

For people, the standards for water quality are specified in Directive No. 2020/2184 European Union 16.12.2020, and in Ordinance No. 9/2001, Official State Gazette, issue 30, about the quality of water intended for drinking purposes, Bulgaria [3–7]. Table 2 lists the parameters for the physicochemical composition.

Table 2. **Parameters used in our studies for physicochemical analysis are Bulgarian State Standard (BDS), ISO, Ordinance No. 9/2001, and additional parameters not included in Ordinance No. 9/2001**

Parameter	Standard	Measuring unit	Maximum limit value
1. pH	BDS EN ISO 10523: 2012	pH values	≥ 6.5 and ≤ 9.5
2. Electrical conductivity	BDS EN 27888: 2000	μS cm^{-1}	2000
3. Calcium (Ca^{2+})	BDS ISO 9964-3 2002	mg L^{-1}	150
4. Sodium (Na^+)	BDS ISO 9964-3: 2002	mg L^{-1}	200
5. Zinc (Zn^{2+})	BDS EN ISO 11885-2009	mg L^{-1}	4
6. Manganese (Mn^{2+})	BDS EN ISO 11885 2009 (item 9.5.3)	μg L^{-1}	50
7. Iron (Fe^{2+})	BDS EN ISO 11885-2009	μg L^{-1}	200
8. Sulfates (SO_4^{2-})	BDS EN ISO 10304-1: 2009	mg L^{-1}	250
9. Chlorides (Cl^{-1})	BDS EN ISO 10304-1: 2009	mg L^{-1}	250
Additional parameters			
10. Potassium (K^+)	BDS ISO 9964-3: 2002	mg L^{-1}	–
11. Hydrogen carbonates (HCO_3^-)	BDS EN ISO 9963-1: 2000	mg L^{-1}	–
12. Carbonates (CO_3^{2-})	BDS EN ISO 9963-1: 2000	mg L^{-1}	–

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The studies with physicochemical indicators were performed in licensed laboratories of Bulgarian and EU standards.

2.2. Fourier transform infrared spectroscopy (FT-IR)

Fourier-IR spectrometer Bruker Vertex was used to research the IR spectra of potassium carbonate.

Thermo Nicolet Avatar 360 Fourier-transform IR has the following parameters: average spectral range: 370–7800 cm^{-1}; visible spectral range 2500–8000 cm^{-1}; resolution: 0.5 cm^{-1}; accuracy of wave number: 0.1 on 2000 cm^{-1}.

2.3. Ceramic element

The investigation was carried out with a 250/90 mm cylindrical ceramic element standardized according to BDS with an active patent BDS 7075–1968. It was made of kaolin and had a filter element EFKTS 90-250 (BDS 7075-68) [8]. The chemical composition of kaolin is Al_2O_3 (52%) SiO_2 (47%) Na_2O (0.3%) K_2O (0.7%) with a pore size of 0.1–0.2 μm. In a 0.9% NaCl solution [9], seawaters from the Black Sea and Aegean Sea were placed in a ceramic element with 337.6 mL of water. The latter was immersed in a beaker containing deionized or river water with a volume of 1414.8 mL. The levels of the liquids in both vessels were initially equalized. The setup was kept hermetically sealed at 22.0 °C.

The scheme of the device [9] for osmosis/diffusion is shown in the Fig. 1.

2.4. Electric device for conductivity

The changes in ionic concentrations in both vessels of the processes of diffusion and osmosis were monitored through the changes in electrical conductivity measured with the fixed AD 76309 probes of two identical ADWA.

2.5. Studies of ion amounts and pH

AD330 EC meters. The amount of sodium ions (Na^+) and pH in both solutions was measured in a certified laboratory (Eurotest Control, Sofia, Bulgaria).

HANNA instruments meter was used for the measurement of pH as well.

3. Results and Review

3.1. Reverse Osmosis

In reverse osmosis's desalination process, seawater is forced through a semi-permeable membrane under pressure significantly exceeding the osmotic pressure difference between fresh and seawater (for seawater 25–50 atm) [10]. Such membranes are domestically produced from polyamide, cellulose nitrate, or cellulose acetate and are available as hollow fibers or rolls [11]. Small water molecules can freely pass through the microspores of these membranes, while larger salt ions and other dissolved substances are retained in the reverse osmosis membrane.

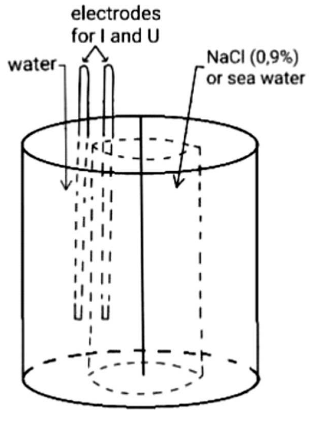

Fig. 1. Scheme of the device for osmosis/diffusion

Today, hundreds of thousands of tons of drinking water are produced worldwide using reverse osmosis. The biggest applications of reverse osmosis for seawater desalination are in China [12], Spain [13], Saudi Arabia [14], *etc.*

The main element of reverse osmosis is the membrane. Depending on their pore size, membranes are used for reverse osmosis, microfiltration, ultrafiltration, and nanofiltration [15].

3.2. Chemical precipitation

In the chemical method of desalination, special precipitating reagents are introduced into seawater. It interacts with the dissolved ions of salts as chlorides and sulfates form insoluble compounds that precipitate [16]. Because seawater contains a large amount of dissolved substances, the consumption of reagents is quite significant and amounts to above 3–5% of the quantity of desalinated water. Substances capable of forming insoluble compounds with sodium (Na^+) and chlorine (Cl^-) ions include silver (Ag^+) and barium (Ba^+) salts [17]. They precipitated silver chloride (AgCl) and barium sulfate (BaSO4) while treating salty water. The reagents are costly, the precipitation reaction with barium salts is slow, and barium salts are toxic. Therefore, chemical precipitation is very rarely used in water desalination.

3.3. Distillation

Water distillation is based on the difference in composition between water and steam formed from it [18, 19]. Special distillation units carry out the process of desalination. The process involves the partial evaporation of water followed by condensation of the vapor. During distillation, the more volatile component (low-boiling) transitions to the vapor phase in greater quantity than the less volatile (high-boiling) component. Therefore, upon condensation, low-boiling components move into the distillate. The high-boiling components remain in the distillation residue. If not one fraction but several ones are distilled from the original mixture, the process is called fractional distillation.

Actually, the biggest application is the fractional-submerged membrane distillation crystallizer technology (FSMDS) [20]. FSMDS is a technology that combines membrane distillation with the crystallization process. This innovative approach to traditional desalination methods offers an effective solution for managing higher salt concentrations. With the membrane distillation method, seawater is pumped into a container where a membrane is submerged. The hydrophobic membrane allows water vapor to pass through but retains the salts and other impurities. The temperature difference between the hot seawater and the cooler side of the membrane (often cooled by ambient air or water) creates a vapor flow through the membrane.

Fractional separation and crystallization occur after the water vapor passes through the membrane and condenses, forming distilled water. In the process, the salt and other minerals remain behind the membrane. Depending on the system design, the salt can be further through crystallization processes, allowing it to be extracted in solid form, which is extremely useful for industrial applications.

FSMDC has the following advantages. This method is more energy-efficient than traditional desalination methods. It utilizes temperature gradients rather than directly heating water. In waste minimization, the crystallization allows for salt extraction in a useful form, reducing water issues. Since the membrane can retain many impurities, the quality of reducing water is high.

This method is particularly suitable for applications where both pure water and salt as a byproduct are needed, such as in industrial or pharmaceutical processes. The hybrid solar-powered membrane distillation (SPMD) is effective in desalinating seawater. This makes it a valuable application in regions, where fresh water is scarce but seawater and sunlight are abundant. Solar energy, collected through solar panels or thermal collectors, is used to heat the seawater. The increased temperature enhances the water's vapor pressure, facilitating its passage through the membrane. The membrane distillation process produces pure water [21].

The method of distillation decreases the amount of deuterium. The average amount of deuterium in drinking water is 156 ppm [22, 23]. For glacier water, there are results less than 125 ppm – Greenland (124.8) [23], Antarctic (89.0), glacier Mappa, and Chilean Andes (91.3 ppm) [5]. The amount of deuterium after distillation ranges from 50 to 125 ppm [24, 25].

3.4. Ion exchange

The ion exchange process for seawater desalination is connected with hydrogen (H^+) and hydroxide ions (OH^-) [26]. This process involves using ion exchange resins, which can replace the cations and anions in seawater with hydrogen and hydroxide ions. This method effectively removes dissolved salts and minerals and converts seawater into drinking water.

The cation exchange resins are loaded with hydrogen ions (H^+) in the cation exchange process. As seawater passes through the resin, cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, are replaced with hydrogen ions from the resin [27, 28]. The anion exchange resins are loaded with hydroxide ions (OH^-) in the anion exchange process. As seawater passes through these resins, the anions in the water, such as (Cl^-), (SO_4^{2-}), and (HCO_3^-), are replaced by hydroxide ions from the resin [27, 28].

The chemical reaction between hydrogen and hydroxide ions, which have been released during the cation and anion exchange, leads to the formation of water:

$$2H^+ + 2OH^- \rightarrow H_2OH^+ + OH^- \rightarrow 2H_2O.$$

Table 3. **Electric parameters – voltage, current, and conductivity of the processes of osmosis/diffusion of seawaters from the Black Sea and Aegean Sea and river water**

Day and time	Voltage, mV	Becher, mS cm^{-1} (diffusion)	Ceramic element, mS cm^{-1} (osmosis)	Difference, mS cm^{-1}	Ratio voltage/ difference
Black Sea/river Vit					
1st day	112.3	32.3	1.17	31.13	3.6
7th day	245.2	20.4	8.24	12.16	22.0
difference	132.9	11.9	7.07	4.83	27.5
Aegean Sea/river Vit					
1st day	168.0	58.3	0.937	57.36	2.9
7th day	338.0	32.4	17.9	14.5	23.3
difference	170.0	25.9	16.96	8.94	19.0

This ion exchange process removes salts from seawater and minimizes the formation of secondary waste. The method is environmentally ecological for desalination. The desalinated water obtained in this way is of high quality and suitable for drinking and other uses.

3.5. Electrodialysis

Electrodialysis (ED) is an electrochemical process desalinating water [25, 26]. It is effective in removing salt from seawater. Electrodialysis uses electric potential to move ions through selective membranes, which are permeable to cations or anions, but not to water or other uncharged molecules. The core components of the electrodialysis system are its ion-exchange membranes, which are arranged alternately between two electrodes (an anode and a cathode). When seawater flows through the channels of the electrodialysis unit, an applied electric field causes the sodium (Na^+) ions and other positively charged ions to move toward the cathode.

When seawater flows through the channels of the electrodialysis unit, an applied electric field causes the sodium (Na^+) and other positively charged ions to move toward the cathode through the cation exchange membranes. Similarly, chloride (Cl^-) and other negatively charged ions move toward the anode through the anion-exchange membranes. This movement separates the ions from the water, thus reducing the salt content and producing desalinated water.

3.6. Osmosis and "blue energy"

Utilizing the osmotic pressure difference between freshwater and seawater, known as "blue energy," offers a renewable method of generating electric energy. In 2009, it was built in Norway Statkraft's osmotic plant [29]. In the last 15 years, the investigations focused on designing and producing semi-permeable membranes optimized for osmotic power. The power density of the membrane has increased from 0.1 to 3 $W \cdot m^{-2}$ [30]. In 2016, an international team achieved a membrane from MoS2 with a power density of 106 $W \cdot m^{-2}$ [31].

Table 4. **Amounts of sodium ions and pH of the process of osmosis in the ceramic element from seawaters from the Black Sea and Aegean Sea**

Samples	Na^+ (mg L^{-1}) Black Sea	pH	Na^+ (mg L^{-1}) Aegean Sea	pH
Control samples before osmosis	4570 ± ± 457	7.53	10830 ± ± 1083	7.08
Samples after osmosis	2055 ± ± 206	7.93	3860 ± ± 386	7.86

Our results are Black Sea – river water osmosis – 3.50 W m^{-2}; Aegean Sea – river water osmosis – 9.64 $W \cdot m^{-2}$

The osmosis and diffusion processes allow for seawater desalination without additional energy. The transfer of ions through a semipermeable membrane generates an electrical potential. The following electric parameters were measured – voltage, current, and conductivity (Table 3).

Table 4 illustrates the amounts of sodium ions and pH of the process of osmosis in the ceramic element from seawaters from the Black Sea and Aegean Sea.

Table 5 shows the amount of sodium ions and pH of the process of diffusion from river Vit, Teteven, Bulgaria

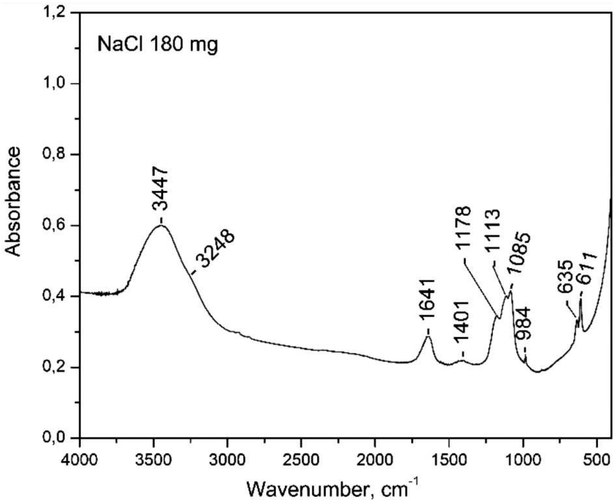

Fig. 2. Results with IR Fourier Spectral Analysis of NaCl
Table 6 illustrates the absorption bands of the IR spectrum

Table 5. **Amount of sodium ions and pH of the process of diffusion from river Vit, Teteven, Bulgaria**

Samples	Na^+ (mg L^{-1})	pH	Na^+ (mg L^{-1})	pH
Control samples before diffusion	<2.0	8.15	<2.0	8.16
Samples after diffusion	2015 ± 201	7.71	4020 ± 402	7.43

Table 6. **Absorption bands in an IR spectrum**

Absorption bands		
Wave number (cm^{-1})	Wavelength (μm)	Type
3447	2.90	Strong
3248	3.08	”
1641	6.09	Weak
1401	7.14	”
1178	8.49	Medium
1113	8.98	”
1085	9.22	”
984	10.16	Weak
635	15.75	”
611	16.37	Medium

The results indicate that the sodium ions in the Black Sea water decreased from 4570 to 2055 mg L^{-1} through osmosis or 55.0%. The reduction in seawater from the Aegean Sea was from 10830 to 3860, or 64.4%. If the water from osmosis is further desalinated for electricity generation, it could yield pure drinking water.

3.7. IR Fourier Spectral Analysis of NaCl

Fig. 2 Shows the results with IR Fourier Spectral Analysis of NaCl.

The peak at 1117 cm^{-1} is typical 0f hexagonal water clusters [32]. This peak exists in NaCl and seawater from the Aegean Sea [33]. The wavelength peak 1117 cm^{-1} exists in an environmental process with water – a dynamic process between the atmosphere and water with solar activity [34] and water filtration with hexagonal structures [35].

4. Conclusions

The following desalination processes have applications in the modern world because of the increasing need for fresh, clean drinking water.

1. Reverse Osmosis. In the reverse osmosis desalination process, seawater is forced through a semipermeable membrane under pressure that significantly exceeds the osmotic pressure difference between fresh and seawater.

2. Chemical precipitation. In the chemical desalination method, specific desalination method, specific precipitating agents are added to seawater. These agents react with dissolved ions, such as chlorides and sulfates, to form insoluble compounds that precipitate out the solution.

3. Distillation. Distillation for water desalination is based on the difference in composition between water and steam it forms. Specialized distillation units perform this process, which involves the partial evaporation of water followed by the condensation of the vapor. During distillation, the more volatile component (low-boiling) transitions to the vapor phase in greater quantity than the less volatile (high-boiling) component.

4. Ion Exchange. The ion exchange process for seawater desalination involves using ion exchange resins to replace the cations and anions in seawater with hydrogen (H^+) and hydroxide ions (OH^-). This method effectively removes dissolved salts and minerals, converting seawater into potable water.

5. Electrodialysis. Electrodialysis is an electrochemical process desalinating water. It effectively removes salts from seawater by using the electric potential to move ions through selective membranes. These membranes are permeable to cations or anions but impervious to water and other uncharged molecules.

The osmotic process allows for the generation of electricity without additional energy expenditure. It is practically implemented with a semi-permeable membrane between seawater and river water.

Up to 64.4% of seawater can be desalinated without additional energy expenditure. The proposal involves lakes with river water and seawater separated by a semi-permeable membrane. Afterward, another desalination method can be used.

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ДЕСОЛОНІЗАЦІЯ МОРСЬКОЇ ВОДИ. ПРОЦЕС ОСМОСУ ДЛЯ “БЛАКИТНОЇ ЕНЕРГІЇ” ТА ОЦІНКА ДЕСОЛОНІЗАЦІЇ

Зроблено порівняльний аналіз методів десолонізації морської води, вказано райони їх застосування та розглянуто проблему отримання енергії в процесі осмосу.

Ключові слова: десолонізація, зворотній осмос, хімічне осадження, дистиляція, осмос з іон-обмінним електродіалізом, “блакитна енергія”.