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Heavy metals separation from geothermal waters for agricultural irrigation

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Abstract: Reverse osmosis (RO) is one of the most widely used technologies for achieving safe water reuse and can be effectively applied in wastewater recovery for crop irrigation. This paper presents the results of research involving the use of a two-stage RO system connected in series to produce water for agricultural use. A critical factor in applying this technology was achieving the target boron concentration. The effectiveness of the technology is also discussed with respect to the heavy metal content of the permeate. Pre-treatment steps, such as pre-filtration, de-ironing, and ultrafiltration (UF), are employed to remove colloidal particles and reduce membrane fouling, thereby enhancing longevity. Previous studies have shown that a two-stage reverse osmosis (RO-RO) system for geothermal water desalination (with initial mineralization of 2.5 g/L) produces permeate with a mineralization of 0.094 g/L and permissible heavy metal concentrations that do not adversely affect the quality or safety of irrigation water. Furthermore, due to the permeate's physicochemical composition, treated geothermal water can be used for drip irrigation without the risk of clogging installations. Future innovations should focus on energy-efficient membrane materials and real-time monitoring to further optimize the desalination process, ensuring sustainable agricultural reuse without soil or crop contamination.

Introduction

In many regions worldwide, limited access to safe drinking water remains a critical challenge, further intensified by population growth, urbanization, and economic development. Although geothermal waters are abundant, their utilization is often constrained by elevated concentrations of heavy metals (e.g., Cd, Pb, and As) and trace elements (e.g., B). To meet the quality standards required for agricultural irrigation, advanced membrane-based separation technologies are necessary. However, this requirement presents significant challenges to the direct use of geothermal water in such applications, particularly in terms of energy consumption and water utilization efficiency. Heavy metals are commonly found in geothermal waters, typically in dissolved form (Briffa et al. 2020). To ensure the safe use of geothermal water for crop irrigation, these contaminants must be effectively removed in accordance with international water quality standards (e.g., WHO, EU) and relevant regulatory guidelines (WHO 2011, Minister of Health 2017, Directive EU 2020).

In many cases, the established limits are extremely low, sometimes in the range of μg/dm³. The presence of heavy metals in water constitutes a significant environmental concern, as it can increase their accumulation in soil, from which plants may subsequently absorb these compounds along with other nutrients (Soleimani et al. 2023). Contamination of both irrigation water and soil with lead or cadmium, particularly when combined with deficiencies in essential nutrients, poses a serious threat to quality and safety of agricultural products. Potassium feldspar-derived adsorbent (PFDA) shows strong potential as a cost-effective alternative to conventional methods for removing heavy metals and mitigating nutrient shortages in irrigation water, thereby providing a sustainable solution and supporting the efficient utilization of potassium feldspar resources (Lin et al. 2024).

As a result of evolving quality standards, increasing anthropogenic pollution, and other threats to crop quality, the concept of precision agriculture (PA) was officially adopted in 2024 by the International Society of Precision Agriculture (ISPA) (Zaman 2023, Salcedo-Arancibia et al. 2024). Environmental pollution caused by human activity has become a global concern. Researchers have confirmed the presence of heavy metals in soil, irrigation water, and cultivated vegetables in Cameroon (Mewouo et al. 2024).

In South Africa, in response to growing global awareness of the importance of water quality monitoring, studies were conducted to assess, among other factors, the presence of heavy metals. The results indicated that water sources in the Rustenburg area are currently safe for agricultural and domestic use. At the same time, the findings highlight the critical importance of continuous monitoring and the risks posed by anthropogenic contamination from various sources (Olagbaju and Wojuola 2024).

In Egypt, studies evaluating the accumulation of heavy metals in soil and agricultural crops irrigated with drain water demonstrated that, to ensure safe contaminant levels, pretreatment in sewage treatment plants is necessary. In particular, concentrations of Co, Cr, and Ni in soils near industrial facilities exceeded background reference levels (Romeh et al. 2025). Furthermore, Khan et al. 2025 emphasized that untreated or insufficiently treated sewage water used for irrigation can increase salinity, nutrient loads, and soil organic matter, as well as contamination risk. Consequently, the urgent development of effective wastewater management and treatment strategies is essential to protect agricultural soils from heavy metal contamination.

Heavy metal contamination requires urgent mitigation, highlighting the crucial role of membrane separation technologies as effective treatment solutions. The use of appropriately selected membrane process parameters, along with the application of improved membranes featuring enhanced selectivity and permeability, can ensure a stable water treatment process that is resistant to fouling and achieves high retention of heavy metals (Alias et al. 2025). Previous studies from various regions worldwide highlight the importance of analyzing water, including wastewater, groundwater, sewage, and geothermal water, prior to its use in crop irrigation. In many cases, these studies highlight the necessity of treatment before reuse (Chaoua et al. 2019, Romeh et al. 2025, Khan et al. 2025, Mizerna et al. 2025). Membrane processes, especially nanofiltration (NF) and reverse osmosis (RO), are effective for the treatment and disinfection of water from diverse sources, including geothermal wastewater (Bodzek et al. 2019).

The article presents the results of an assay aimed at examining the removal efficiency of heavy metals from geothermal wastewater using a two-stage RO-RO system connected in series on a semi-industrial scale. This configuration was designed to achieve low boron concentration in the treated water (Tomaszewska and Bodzek 2013a, Tomaszewska and Bodzek 2013b). The water used in the experiments was characterized by elevated mineralization, approximately 2.5 g/L. All processes were conducted at a semi-industrial scale under optimized process parameters.

Materials and methods

Apparatus

The semi-industrial water treatment plant was designed with a technological system comprising three primary stages, each aligned with the specific function of the installed equipment: (1) initial water pre-treatment, (2) main treatment using an RO-RO connected in series, and (3) final conditioning to ensure water quality suitable for agricultural irrigation. The feed water temperature was set to 30±1°C. The duration of the water treatment process was 24 hours. The study presents the results of the first experiment conducted to investigate water extraction for agricultural use.

The general layout of the treatment system is illustrated in Figure 1. The pre-treatment phase employed a set of devices, indicated in blue in Figure 1, including a mechanical filter, an iron removal unit, and an UF module. These components serve to prepare raw geothermal wastewater for subsequent high-pressure membrane-based processes, ensuring the protection and efficient performance of sensitive filtration membranes by removing suspended solids and other potential foulants. The iron removal system is equipped with an automated rinsing function that activates periodically to flush out accumulated contaminants (Tomaszewska and Bodzek 2013a, Tomaszewska and Bodzek 2013b). This backwashing process is fully controlled by an automatic system. In the final step of pre-treatment, following mechanical filtration and iron removal, the water passes through the UF module, which is equipped with a UF membrane manufactured by DOW FILMTEC.

The second key stage of the treatment process involved a two-stage RO-RO desalination system, employing membranes arranged in series, along with a module for pH adjustment of the permeate from both the first and second stages. The pH was adjusted to 5.5 prior to RO-1 using HCl and subsequently corrected to 10 before RO-2 using NaOH (Figure 1). In the final stage, additional pH adjustment was performed in accordance with the requirements for irrigation water quality. This operational strategy represented a key factor in reducing boron concentration in the permeate (Kabay et al. 2013, Tomaszewska and Bodzek 2013a, Tomaszewska and Bodzek 2013b, Jarma et al. 2021). The RO units were equipped with BW30FR-400 membranes (DOW FILMTEC), which are thin-film composite polyamide membranes (Product Card – BW30FR-4000 membrane). The permeate produced by the first RO unit served as the feed water for the second unit. The system operated at a permeate recovery rate of 60%, with operating pressures maintained at 11 bar for the first RO stage and 10 bar for the second stage. The geothermal feed water flow rate entering the desalination system ranged from 4 to 5 m^3/h, with an average of approximately 4.5 m^3/h. In the final treatment step, the RO permeate underwent additional ultraviolet (UV) disinfection to eliminate potential microbial contaminants (Tomaszewska and Bodzek 2013a, Tomaszewska and Bodzek 2013b, Tomaszewska ed. 2018). This step completed the geothermal water treatment process. An automated control system governed the operation of individual components, ensuring coordinated and efficient functioning throughout the treatment sequence. Given the research-oriented nature of the installation, the system was additionally equipped with monitoring instrumentation and sampling ports at key locations, enabling the collection of operational data and water samples for laboratory-based physicochemical analyses. Following both RO stages, permeate samples were collected via sampling taps and analyzed in an accredited laboratory to assess water quality parameters.

Geothermal water

The concentrations of heavy metals in geothermal wastewater (used for heating purposes) were determined in an accredited

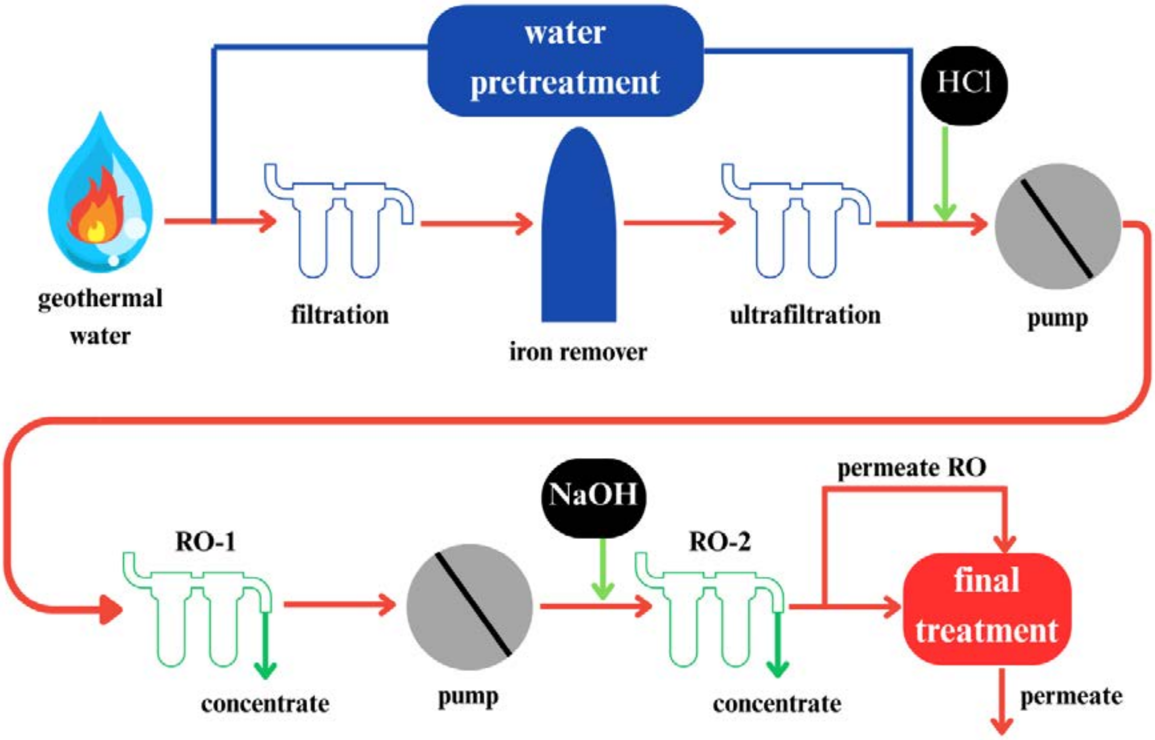

Fig 1. Scheme of the water treatment installation including UF/RO-1/RO-2 processes

laboratory in accordance with current international standards, using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). Table 1 shows the concentrations of heavy metals in raw geothermal water used for membrane tests, compared with drinking water standards established by WHO, EU directives, and national (Polish) legislation (WHO 2011, Minister of Health 2017, Directive EU 2020), as well as the guidelines provided by Flood (1996) and Bailey (1999). Water quality for irrigation is often benchmarked against drinking water standards due to the absence of strict regulatory limits for irrigation water and to ensure plant and soil safety.

Analysis method of water quality

To evaluate the performance of semi-industrial-scale process, the retention coefficients (R,[%) of heavy metals were calculated based on the following equation:

$$R = \left(1 - \frac{C_p}{C_n}\right) \cdot 100\%$$

where: R – the retention coefficient [%]; C_p – the concentration of a given parameter in the permeate [mg/L]; C_n – the concentration of the corresponding parameter in geothermal wastewater [mg/L].

Permeate suitability for agricultural irrigation – heavy metals content

The suitability of the permeate for irrigation purposes, with particular emphasis on heavy metal content, was assessed by comparison with drinking water standards established by the WHO, EU directives, and national (Polish) regulations (WHO 2011, Minister of Health 2017, Directive EU 2020), as well as the guideline values reported by Flood (1996) and Bailey (1999) (Table 1).

Results

Following the semi-industrial tests using the proposed treatment system, the retention coefficients of heavy metals were calculated (Table 2). For most analyzed heavy metals, retention coefficients exceeding 99.9% were achieved, confirming the near-complete removal of these constituents from the treated water. Only mercury (Hg) exhibited a retention coefficient of zero; however, this does not compromise the quality of the resulting permeate, as the concentration of mercury in the raw geothermal wastewater remained within acceptable limits. For waters containing elevated mercury concentrations , additional treatment steps may be necessary to meet specific quality standards. The symbol '-' indicates that the retention coefficient for a given element could not be calculated because its concentration in the raw geothermal water was below the detection limit.

Table 3 presents the results of the physicochemical analyses of the permeate, as well as the permeate supplemented with a nutrient solution (safe for crops and human health), applied at a dosage adjusted to the permeate parameters, primarily pH and EC values.

The experiment aimed to produce treated geothermal water with properties suitable for agricultural irrigation. Accordingly, based on the legal regulations outlined in Table 1, as well as relevant recommendations, the quality of both the permeate and the nutrient-enriched permeate (with adjusted pH) was evaluated in terms of their suitability for crop irrigation. Based on the obtained results, as well as the requirements and recommendations provided by researchers and Polish, WHO, and EU regulations, it was decided to supplement the treated geothermal water with an appropriate dose of nutrients and

Table 1. Concentration of heavy metals in geothermal wastewater against the background of drinking water standards defined by WHO, EU directives, and national (Polish) legislation (WHO 2011, Minister of Health 2017, Directive EU 2020), as well as the guidelines provided by Flood (1996) and Bailey (1999).

Element [mg/L]	Geothermal wastewater	WHO standard [mg/L] (WHO 2011)	EU standards [mg/L] (Directive EU 2020)	Regulation of the Polish Minister of Health [mg/L] (Minister of Health 2017)	Flood (1996), Bailey (1999)
TDS	**2351.50**	500	-	-	-
EC [mS/cm]	**3.67**	-	2.5	2.5	1.1
pH	6.9	6.5 - 8.5	6.5 – 9.5	6.5 – 9.5	5 - 7
Cu	0.01	2.0	2.0	2.0	0.08 – 0.15
Se	<0.001	0.04	0.01	-	-
As	**0.013**	0.01	0.01	0.01	0.01
Cr	<0.005	0.05	0.05	0.05	0.1
Cd	<0.0003	0.003	0.003	0.003	0.01
Ni	<0.001	0.07	0.02	0.02	0.2
Pb	0.0045	0.01	0.01 (from January 1, 2036, reduced to 0.005)	0.01	0.015
Hg	0.0003	0.006	0.001	0.001	0.001

HCl solutions. The pH was adjusted to 6.5 by adding 500 mL of an HCl solution—prepared by dissolving 10 mL of HCl in 1 L of distilled water. This approach aimed to decrease the pH of the treated geothermal water and increase the concentration of essential ions required for agricultural cultivation (nutrient addition), while simultaneously maintaining low levels of heavy metals.

Based on the data presented in Table 4, all analyzed elements (heavy metals) meet the requirements set by WHO, EU, and Polish regulations, as well as the recommended values reported by previous studies. The addition of HCl reduced the pH to levels suitable for drinking water and irrigation purposes. Furthermore, the supplementation with a nutrient solution—applied at a dosage adjusted to the pH and EC values—resulted in a mixture with a total dissolved solids

Table 2. The calculated retention coefficients R [%] of heavy metals for the analyzed permeate.

Element R [%]	Permeate
TDS	96.8
Cu	> 99.9
Se	-
As	> 99.9
Cr	-
Cd	-
Ni	-
Pb	> 99.9
Hg	0

Table 3. The concentration of heavy metals in the obtained permeate and permeated with nutrient addition.

Element [mg/L]	Permeate	Permeate with added nutrition - adjusted for irrigation
TDS	93.8	618.3
EC [mS/cm]	0.339	1.766
pH	11.1	6.5
Cu	<0.001	0.119
Se	<0.001	<0.001
As	<0.001	<0.001
Cr	<0.005	<0.005
Cd	<0.0003	<0.0003
Ni	<0.001	<0.001
Pb	<0.0001	0.0007
Hg	0.0003	0.0003

Table 4. The evaluation of the fulfillment of drinking water requirements and recommendations for irrigation purposes was conducted following WHO, EU and Polish regulations as well as according to Flood (1996) and Bailey (1999) recommendations (Flood 1996, Bailey et al. 1999, WHO 2011, Minister of Health 2017, Directive EU 2020).

Element [mg/L]	WHO standard [mg/L] (WHO 2011)	EU standards [mg/L] (Directive EU 2020)	Regulation of the Polish Minister of Health [mg/L] (Minister of Health 2017)	Flood (1996), Bailey (1999)	Permeate	Permeate with added nutrition - adjusted for irrigation
TDS	600	-	-	-	within	slightly above
EC [mS/cm]	-	2.5	2.5	1.1	within	within
pH	6.5 - 8.5	6.5 – 9.5	6.5 – 9.5	5 - 7	above	within
Cu	2.0	2.0	2.0	0.08 – 0.15	within	within
Se	0.04	0.01	-	-	within	within
As	0.01	0.01	0.01	0.01	within	within
Cr	0.05	0.05	0.05	0.1	within	within
Cd	0.003	0.003	0.003	0.01	within	within
Ni	0.07	0.02	0.02	0.2	within	within
Pb	0.01	0.01 (from January 1, 2036 reduced to 0.005)	0.01	0.015	within	within
Hg	0.006	0.001	0.001	0.001	within	within

(TDS) concentration slightly above the recommended value for high-quality water. This minor exceedance is not expected to adversely affect crop quality, even for plants sensitive to water salinity.

Based on the obtained results, it can be concluded that heavy metal ions, even at low concentrations, can be effectively removed from aqueous solutions using RO, specifically a two-stage RO-RO system (Tomaszewska and Bodzek 2013a, Tomaszewska and Bodzek 2013b). The membrane used in the process retained the majority of dissolved salts (Bodzek and Konieczny 2011a, Bodzek and Konieczny 2011b, Tomaszewska and Bodzek 2013a, Tomaszewska and Bodzek 2013b, Tomaszewska ed. 2028, Tyszer and Tomaszewska 2021, Tyszer et al. 2021). However, in cases where the retention coefficient of a specific heavy metal is insufficient, additional treatment methods may be required (Korus et al. 2020). Activated carbon, for example, can significantly enhance the removal efficiency of metal cations, with mercury showing particularly high adsorption potential. For higher concentrations of metals (above 500 mg/L), electrodialysis may be used, whereas at low concentrations (below 5 mg/L), biosorption or ion exchange can be applied. However, the use of these complementary methods may alter physicochemical properties, potentially causing non-compliance with irrigation or drinking water standards (Dębowski and Lach 1996, Bodzek and Konieczny 2011a, Bodzek and Konieczny 2011b, Zaman et al. 2018). Alternative selective removal techniques have also been reported. Sapropel has been used to remove cadmium, chromium, copper, and zinc from aqueous solutions, achieving removal rates of 84–93% depending on the metal, with contact time ranges from 15 to 60 minutes (Albrektiene-Placake and Paliulis 2024). Deep eutectic solvents (DESs) have been applied in both solvent extraction and membrane processes for metal iron removal from various aqueous solutions (Kaczorowska and Bożejewicz (2025) . Pb (II) removal efficiencies up to 99% have been demonstrated using Theobroma cacao L. as a bioadsorbent in packed columns under optimized conditions (Tejada Tovar et al. 2025). Thaçi et al. (2025) stated that lignite is an effective raw material for the adsorption of Pb (II) and Cd (II) ions from aqueous solution, with 0.5M hydrochloric acid being the most effective regenerating agent (Thaçi et al. 2025). Biosorption using algal cultures has been explored as well. Cyganowska (2023) examined a pure culture of *Raphidocelis subcapitata* and a mixed *chlorophyta* population for copper and lead removal from industrial wastewater generated in battery manufacturing. Longer contact times increased removal efficiency, with an optimum duration of 1 hour. Although removal rates of 43-72% were achieved, the author noted that process efficiency could be further improved by adjusting the pH.

Membrane filtration, particularly ultrafiltration (UF) and microfiltration (MF), can support and enhance the disinfection of water and biologically treated wastewater, while nanofiltration (NF) and reverse osmosis (RO) can serve as primary treatment methods for geothermal waters (Bodzek et al. 2019). Based on the present experiment, geothermal waters represent a potentially high-quality alternative water source that, after appropriate treatment, can be used for crop irrigation. These waters exhibit a relatively stable physicochemical composition and are generally free from anthropogenic or biological contamination. In contrast, pre-treated wastewater from conventional treatment plants may pose a contamination risk for crops (Chaoua et al. 2019, Romeh et al. 2025, Khan et al. 2025, Mizerna et al. 2025).

Despite being used for energy production, geothermal wastewaters in their natural state may contain slightly elevated concentrations of certain heavy metals. However, the proposed treatment system enabled the production of high-quality permeate that is safe for both plants and soil in terms of heavy metal content. Researchers from Turkey have also demonstrated that spent geothermal water, when treated using integrated pressure-driven separation processes, can be safely reused for agricultural irrigation. They emphasized that properly designed systems incorporating pressure-driven membranes allow the reuse of geothermal water, reducing the demand on conventional drinking water sources (Jarma et al. 2022a, Jarma et al. 2022b). Consequently, the use of renewable energy sources to treat geothermal water for agricultural irrigation can reduce the sector's reliance on fossil energy (Tomaszewska et al. 2021).

Conclusions

This study aimed to evaluate the efficiency of heavy metal removal from geothermal wastewater on a semi-industrial scale using a two-stage RO-RO module connected in series, with the goal of producing permeate suitable for agricultural irrigation. The use of untreated geothermal wastewater for irrigation can increase heavy metal concentrations in crops, particularly due to the naturally elevated arsenic levels . Treating geothermal wastewater to produce water suitable for irrigation is therefore a promising solution, especially in the context of climate change, which is leading to longer and more frequent droughts and expanding areas at risk of water scarcity.

This article presents the results of experiments assessing the potential reuse of geothermal wastewater permeate, generated by a properly designed and optimized desalination system, as an alternative water resource for agricultural applications. The wastewater, originating from geothermal heating operations, was subjected to membrane-based treatment under controlled process conditions. Pre-treatment of raw water in the semi-industrial process played an important role in ensuring the effective retention of the analyzed components.

Based on the results obtained, the treated water complies with the quality criteria specified in the Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption (Journal of Laws of 2017, item 2294 - Minister of Health 2017) and meets the recommendations for irrigation purposes.

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Separacja metali ciężkich z wód geotermalnych na potrzeby nawadniania w rolnictwie

Streszczenie: Odwrócona osmoza (RO) jest jedną z najczęściej stosowanych technologii umożliwiających bezpieczne ponowne wykorzystanie wody. Technologia ta może być stosowana do odzysku wód odpadowych w nawadnianiu upraw. W niniejszym artykule przedstawiono wyniki badań dotyczących wykorzystania dwustopniowego systemu odwróconej osmozy (RO) połączonego szeregowo w celu uzyskania wody do zastosowań rolniczych. Kluczowym elementem zastosowania tej technologii było osiągnięcie oczekiwanego stężenia boru. W artykule omówiono skuteczność technologii w odniesieniu do zawartości metali ciężkich w permeacie. Etapy wstępnego uzdatniania, takie jak wstępna filtracja, odżelazianie oraz ultrafiltracja (UF) w celu usunięcia cząstek koloidalnych i zmniejszenia zanieczyszczenia membran, zwiększają trwałość membran. Badania wykazują, że zastosowanie dwustopniowego systemu odwróconej osmozy (RO-RO) do odsalania wód geotermalnych (o początkowej mineralizacji 2,5 g/L) pozwala uzyskać permeat o mineralizacji 0,094 g/L oraz dopuszczalnych stężeniach metali ciężkich, które nie wpływają na jakość ani bezpieczeństwo nawadniania upraw. Dodatkowo, dzięki fizykochemicznemu składowi permeatu, uzdatnioną wodę geotermalną można stosować do nawadniania kropelkowego bez ryzyka zatkania instalacji. Przyszłe innowacje powinny koncentrować się na energooszczędnych materiałach membranowych oraz monitorowaniu w czasie rzeczywistym, aby jeszcze bardziej zoptymalizować proces odsalania, zapewniając zrównoważone ponowne wykorzystanie wody w rolnictwie bez ryzyka skażenia gleby lub upraw.