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POSSIBILITIES FOR REDUCING THE HARDNESS OF REVERSE OSMOSIS WASTEWATER AND ITS APPLICATION AS A LIQUID FERTILIZER FOR AGRICULTURAL CROPS

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Abstract

This study investigates the possibilities of reducing the hardness of highly mineralized wastewater generated as a result of reverse osmosis (RO) technology and reprocessing it for use as a liquid fertilizer. As the object of the research, wastewater obtained from the RO unit of Soda Workshop No. 3 at JSC "Ferganaazot" was selected. The high concentrations of calcium and magnesium ions in RO wastewater make its direct discharge into the environment environmentally hazardous; however, the presence of potassium and nitrogen-containing compounds turns this water into a promising resource for use as a liquid fertilizer in agriculture.

Since the high hardness of the wastewater limits this possibility, KU-2/8 cation-exchange and AB-17/8 anion-exchange resins were used to reduce hardness. Experiments were conducted under laboratory conditions using individual cation-exchange, anion-exchange, and mixed-bed (FSD) systems. The chemical composition of the water samples was analyzed in terms of pH, total hardness, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO^{3-}, NH^{4+}, K^+, Na^+, and other ions.

The obtained results showed that the KU-2/8 cation-exchange resin reduced total hardness from 42 mg eq/dm³ to 1.25 mg eq/dm³ in the first cycle and effectively removed Ca^{2+} and Mg^{2+} ions. Although the AB-17/8 anion-exchange resin significantly reduced SO_4^{2-} and NO^{3-} ions, it was found to undergo rapid degradation under conditions of strong alkaline regeneration. Using the mixed-bed (FSD) system, total water hardness was reduced to 0.45 mg eq/dm³; however, excessive demineralization of the water led to a decrease in the content of beneficial macroelements.

Keywords: *Reverse osmosis wastewater; ion-exchange resins; KU-2/8 cation exchanger; AB-17/8 anion exchanger; water hardness; mixed-bed (FSD) system; RO concentrate; regeneration*

Introduction

Osmosis technologies, particularly reverse osmosis (RO), are widely used in industrial and municipal water treatment. Although this technology is highly efficient, the wastewater it generates (RO concentrate or brine) may have adverse environmental impacts. RO wastewater is often characterized by high hardness, alkalinity, and elevated concentrations of ions such as sulfates and nitrates, and its direct discharge into natural water bodies can cause damage to ecosystems (Smith, J., et al., 2022, 115–130; Li, X., & Zhao, Y., 2021, 117–125: Nguyen, T., et al., 2020; 122–135., Kumar, R., et al., 2023, 139–152; Chen, L., et al., 2021, 233–245).

However, the composition of RO wastewater includes not only harmful substances but also macroelements beneficial for soil and plant growth, such as potassium (K^+) and nitrogen (NO^{3-}, NH_4^+). Reverse osmosis wastewater has a high ionic concentration, and when used directly for irrigation, elevated levels of Na^+ and SO_4^{2-} may induce stress in plants (Khamdamova, Z. Sh., Sherkuziev, D. Sh., Khamdamov, D. M., 2025, 454–460). Therefore, converting RO wastewater into a liquid fertilizer instead of direct discharge represents a more beneficial and environmentally safe solution for both industry and agriculture (Patel, M., et al., 2022, 58–68; Wang, H., & Li, J., 2020, 1123–1135; Zhang, Q., et al., 2021, 101–112; Das, P., et al., 2022, 4123–4135; Sato, K., & Tanaka, H., 2020, 115–124).

Nevertheless, RO wastewater typically exhibits high hardness (reaching 42 mg eq/dm^3 in this study), which limits its application as a liquid fertilizer. High water hardness can negatively affect soil structure and disrupt ionic balance in plants.

Consequently, reducing water hardness is a necessary step before utilizing RO wastewater as a fertilizer (Lee, S., et al., 2023, 345–358; Ahmed, R., et al., 2021, 67–79; Park, D., et al., 2022, 204–215; Silva, C., et al., 2020, 104–115; Huang, Y., et al., 2021, 108–119).

The reduction or elimination of water hardness is currently an important issue from ecological, economic, and sanitary perspectives (Chen, L., et al., 2019, 102–112; Missimer, T. M., 2018, 1–12; Khamdamova, Z. Sh., Sherkuziev, D. Sh., Khamdamov, D. M., 2025, 240–250). As a solution to this problem, attention was focused on ion-exchange resins.

Ion-exchange resins (KU-2/8 cation exchanger and AB-17/8 anion exchanger) were selected to perform this task. These resins effectively remove hardness-forming ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-} from RO wastewater, thereby reducing water hardness and creating suitable conditions for liquid fertilizer preparation. The research results indicate that although the resins effectively purify the water composition, excessive treatment – namely, the removal of all ions – also reduces beneficial elements such as potassium and nitrogen. As a result, the treated water does not reach an optimal state for use as a liquid fertilizer. In addition, practical limitations were identified, including the degradation of the anion-exchange resin after strong alkaline regeneration and its lack of operational stability (Martinez, A., et al., 2022, 120–132; Roberts, G., et al., 2020, 456–469; Wang, Z., & Chen, X., 2021, 89–101., Kim, S., et al., 2022, 121–132; Johnson, P., & Lee, H., 2023, 102–115).

Thus, in order to reuse RO wastewater as a liquid fertilizer, it is necessary to reduce its hardness; however, the application of ion-exchange methods may remove not only harmful components but also beneficial elements, which requires optimization and a balanced approach. In this context, the present study is aimed at determining an optimal method that enables effective hardness removal from RO wastewater using KU-2/8 and AB-17/8 resins while preserving its suitability for subsequent liquid fertilizer production.

Practical significance

Direct discharge of RO wastewater into the natural environment is harmful; however, reducing its hardness through ion exchange creates favorable conditions for liquid fertilizer production. At the same time, excessive treatment may also eliminate beneficial elements; therefore, identifying an optimal balance is crucial (Patel, M., et al., 2022, 58–68; Wang, H., & Li, J., 2020, 1123–1135; Zhang, Q., et al., 2021, 101–112; Das, P., et al., 2022, 4123–4135; Sato, K., & Tanaka, H., 2020, 115–124; Kim, S., et al., 2022, 121–132; Johnson, P., & Lee, H., 2023, 102–115; Zhang, L., et al., 2021, 116–128., Li, H., & Xu, Y., 2022, 132–145).

Experiments and methods

Experimental Object and Materials Used

Experimental studies were carried out using wastewater (concentrate) generated by a reverse osmosis (RO) unit operating at the Water Treatment and Neutralization Workshop of JSC "Ferganaazot", located in the Fergana region. This wastewater is characterized by high mineralization and elevated concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sulfate (SO_4^{2-}), and nitrate (NO^{3-}) ions. For this reason, the direct discharge of this wastewater into the environment poses a significant ecological risk.

To perform ion-exchange processes, the widely used industrial ion-exchange resins KU-2/8 (cation exchanger) and AB-17/8 (anion exchanger) were selected. Both resins had a granulometric particle size of 0.315 mm, which ensures efficient mass transfer. Each resin was separately measured in an amount of 50 cm³ and packed into glass columns with a diameter of d = 25.0 ± 0.1 mm and a height of h ≤ 800 mm. All experiments were conducted under laboratory conditions.

Preparation and Regeneration of Resins

Prior to the experiments, the ion-exchange resins were soaked in distilled water for 8 hours for activation purposes. This step ensured complete swelling of the resin granules and the opening of active ion-exchange sites. After soaking, the resins were carefully loaded into the prepared columns, avoiding the formation of air bubbles.

The packed columns were rinsed with 0.5 L of distilled water at a flow rate of 250 cm³/h in a dropwise mode. This procedure served to remove residual mechanical impurities and contaminants remaining from the manufacturing process.

To restore the ion-exchange capacity of the resins, a regeneration process was carried out under the following conditions:

KU-2/8 cation-exchange resin was regenerated using 100 mL of a 4% sulfuric acid (H_2SO_4) solution;

AB-17/8 anion-exchange resin was regenerated using 175 mL of a 4% sodium hydroxide (NaOH) solution.

The regeneration flow rate was maintained at 250 cm³/h. After regeneration, the resins were rinsed with distilled water until a neutral medium (pH ≈ 7) was achieved. Neutralization was monitored using indicator paper. Upon completion of neutralization, the resins in the columns were kept in a closed state filled with distilled water for 1 hour to ensure the complete completion of the regeneration process.

Figure 1. *Experimental setup and methodologies*

Chemical Analysis Methods

To determine the quality of the water samples treated by the ion-exchange process and to assess changes in the concentrations of major ions, comprehensive chemical analyses were performed. The analyses included the following parameters:

- hydrogen ion concentration (pH);
- total hardness;
- calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions;
- sulfate (SO_4^{2-}), nitrate (NO^{3-}), nitrite (NO_2^-), and ammonium (NH_4^+) ions;
- sodium (Na^+) and potassium (K^+) ions;
- chloride (Cl^-) ions;
- iron (Fe^{3+}) ions.

Water samples collected after each regeneration cycle were gathered separately and analyzed using standard analytical methods.

Potentiometric, complexometric, titrimetric, flame photometric, mercurimetric, and photocolorimetric methods were employed for the analyses. All analyses were carried out at the Central Chemical Laboratory of the "Ferganaazot" plant.

Experimental section and results

Experiments conducted using KU-2/8 cation-exchange resin and AB-17/8 anion-exchange resin were performed by passing reverse osmosis (RO) wastewater (concentrate) from the RO unit of Soda Workshop No. 3 through the resins at a flow rate of 250 cm³/h. Prior to the experiments, the resins were kept in a closed state filled with distilled water for 1 hour.

The first 100 mL of filtrate was discarded, as it was considered non-equilibrated water that had not yet reached ion-exchange equilibrium with the resin. In subsequent stages, the collected filtrates were gathered separately according to volume, and their total hardness and chemical composition were determined.

Table 1. *Total hardness values of water at each stage after treatment with KU-2/8 cation-exchange resin and AB-17/8 anion-exchange resin*

No.	KU-2/8 Cation-Exchange Resin		AB-17/8 Anion-Exchange Resin	
	Volume of water passed through the resin, mL	**Total hardness, mg eq/dm³**	**Volume of water passed through the resin, mL**	**Total hardness, mg eq/dm³**
1.	50	0.25	50	8,2
2.	100	0.17	100	7,8
3.	200	0.04	200	9,2
4.	200	0.07	200	9,2
5.	300	0.04	200	10,4
6.	500	0.07		
7.	500	0.2		
8.	500	16.9		

The KU-2/8 cation-exchange resin effectively removed Ca^{2+} and Mg^{2+} ions, while the AB-17/8 anion-exchange resin reduced SO_4^{2-} and NO_3^- ions. During the first cycle, the water hardness was reduced to the target level.

However, since the total hardness values obtained after treatment with the KU-2/8 cation-exchange and AB-17/8 anion-exchange resins exceeded the required threshold, the purification process was stopped. A second regeneration was then carried out following the same regeneration procedure described above. The treated and collected water samples that passed through the KU-2/8 cation-exchange and AB-17/8 anion-exchange resins were subsequently subjected to chemical analysis. The measurement results were recorded in tabular form, and the efficiency of the ion-exchange process was evaluated (Table 2).

Figure 2. *Samples obtained under laboratory conditions*

Table 2. *General analytical parameters of water samples before and after treatment with KU-2/8 cation-exchange resin and AB-17/8 anion-exchange resin*

No.	Parameters	Results		
		Soda Workshop No.3 Wastewater	KU-2/8 Cation-Exchange Resin	AB-17/8 Anion-Exchange Resin
1.	Hydrogen ion concentration (pH)	7.86	6.07	11.48
2.	Magnesium ions (Mg^{2+}), mg eq/dm^3	17.0	1.05	0.65
3.	Calcium ions (Ca^{2+}), mg eq/dm^3	25.0	0.2	4.85
4.	Total hardness, mg eq/dm^3	42.0	1.25	5.5
5.	Total alkalinity, mg eq/dm^3	22.0	0.3	15.5
6.	Sodium ion mass concentration (Na^+), mg/dm^3	0.13	0.35	0.13
7.	Potassium ion mass concentration (K^+), mg/dm^3	16.3	8.2	15.7
8.	Chloride ion mass concentration (Cl^-), mg/dm^3	31.9	28.36	58.4
9.	Nitrite ion mass concentration (NO_2^-), mg/dm^3	0.0	0.645	0.0
10.	Nitrate ion mass concentration (NO_3^-), mg/dm^3	56.0	34.0	10.0
11.	Ammonium ion mass concentration (NH_4^+), mg/dm^3	0.0	0.0	0.0
12.	Iron (Fe^{3+}) ion mass concentration, mg/dm^3	0.06	0.18	0.07
13.	Sulfate ion mass concentration (SO_4^{2-}), mg/dm^3	1152.0	918.7	1.044

The KU-2/8 cation-exchange resin effectively reduced water hardness, while the AB-17/8 anion-exchange resin increased alkalinity and almost completely removed SO_4^{2-} ions.

Mixed-Bed (FSD) Ion-Exchange System

To achieve deeper water purification and maximize hardness removal, a mixed-bed (FSD – *Filtr Smeshannogo Deystviya*) ion-exchange system was employed. In this stage, water that had passed through the KU-2/8 cation-exchange resin was passed through a column containing freshly regenerated AB-17/8 anion-exchange resin.

In the FSD system, the first 100 mL of filtrate was discarded, as it represented non-equilibrated water that had not yet reached ion-exchange equilibrium with the resin. Subsequently, the filtrates were collected separately according to volume, and their total hardness and chemical composition were determined (Table 3).

Table 3. *Total hardness values of water at each stage after passing through the FSD resin*

No.	Volume of water passed through FSD resin, mL	Total hardness, mg eq/dm³
1.	100	0.13
2.	100	0.174
3.	200	0.18
4.	200	0.38

The mixed-bed (FSD) system reduced the total hardness to a minimum level (0.45 mg eq/dm³), while partially preserving beneficial K^+ and NO_3^- ions.

Table 4. *General analytical parameters of water samples before and after treatment with FSD resin*

No	Parameter	Results	
		Soda Workshop No. 3 Wastewater	FSD resin
1.	Hydrogen ion concentration (pH)	7.86	12.14
2.	Magnesium ions (Mg^{2+}), mg eq/dm³	17.0	0.15
3.	Calcium ions (Ca^{2+}), mg eq/dm³	25.0	0.3
4.	Total hardness, mg eq/dm³	42.0	0.45
5.	Total alkalinity, mg eq/dm³	22.0	19.25
6.	Sodium ion mass concentration (Na^+), mg/dm³	0.13	376.9
7.	Potassium ion mass concentration (K^+), mg/dm³	16.3	13.5
8.	Chloride ion mass concentration (Cl^-), mg/dm³	31.9	124.9
9.	Nitrite ion mass concentration (NO_2^-), mg/dm³	0.0	0.01
10.	Nitrate ion mass concentration (NO_3^-), mg/dm³	56.0	0.43
11.	Ammonium ion mass concentration (NH_4^+), mg/dm³	0.0	0.0
12.	Iron (Fe^{3+}) ion mass concentration, mg/dm³	0.06	0.0
13.	Sulfate ion mass concentration (SO_4^{2-}), mg/dm³	1152.0	43.8

Using the mixed-bed system, a sharp decrease in the concentrations of Ca^{2+} and Mg^{2+} ions, as well as SO_4^{2-} and NO_3^- ions, was observed. At the same time, the high degree of water demineralization indicated the need to assess its suitability for use as a liquid fertilizer.

Experiments conducted after the 2nd, 3rd, and 4th regenerations of the KU-2/8 cation-exchange resin showed that after the 2nd regeneration, the KU-2/8 cation-exchange resin was washed with 330 mL of distilled water until it reached a neutral state. The KU-2/8 cation-exchange resin was then ready for reuse. Subsequently, the wastewater concentrate was passed through the resin again. The first 100 mL of filtrate was discarded. The volume and total hardness of water passing through the resin at each subsequent stage were determined and recorded.

Table 5. *Analysis of total hardness of water passing through KU-2/8 resin after the 2nd regeneration*

No.	Volume of water passed through KU-2/8 cation-exchange resin after 2nd regeneration, mL	Total hardness, mg eq/dm³
1.	50	0.7
2.	100	1.09
3.	300	0.85
4.	200	0.84
5.	200	15.2

The purification process was stopped because the total hardness of water passing through the KU-2/8 cation-exchange resin exceeded the desired value (15.2 mg eq/dm³). A third regeneration was then carried out following the previously described procedure. The treated and collected water (KU2R) passing through the KU-2/8 cation-exchange resin was subjected to chemical analysis.

After the 3rd regeneration, the KU-2/8 cation-exchange resin was washed with 300 mL of distilled water until it reached a neutral state. The resin was then ready for a third use. The wastewater concentrate was passed through the resin again. The first 100 mL of filtrate was discarded. The volume and total hardness of water passing through the resin at each subsequent stage were determined and recorded.

Table 6. *Analysis of total hardness of water passing through KU-2/8 resin after the 3rd regeneration*

No.	Volume of water passed through KU-2/8 cation-exchange resin after 3rd regeneration, mL	Total hardness, mg eq/dm³
1.	100	2.93
2.	100	4.6
3.	200	4.0
4.	250	4.7
5.	300	30.6
6.	100	30.75

The purification process was stopped because the total hardness of water passing through the KU-2/8 cation-exchange resin exceeded the desired value (30.75 mg eq/dm³). A fourth regeneration was carried out following the previously described procedure. The treated and collected water (KU3R) passing through the KU-2/8 cation-exchange resin was subjected to chemical analysis.

After the 4th regeneration, the KU-2/8 cation-exchange resin was washed with 300 mL of distilled water until it reached a neutral state. The resin was then ready for a fourth use. The wastewater concentrate was passed through the resin again. The first 100 mL of filtrate was discarded. The volume and total hardness of water passing through the resin at each subsequent stage were determined and recorded.

Table 7. *Analysis of total hardness of water passing through KU-2/8 resin after the 4th regeneration*

No.	Volume of water passed through KU-2/8 cation-exchange resin after 4th regeneration, mL	Total hardness, mg eq/dm³
1.	100	4.1
2.	100	4.25
3.	200	4.3
4.	300	6.0
5.	300	17.5

The purification process was stopped because the total hardness of water passing through the KU-2/8 cation-exchange resin exceeded the desired value (17.5 mg eq/dm³). The treated and collected water (KU 4 R) passing through the KU-2/8 cation-exchange resin was subjected to chemical analysis.

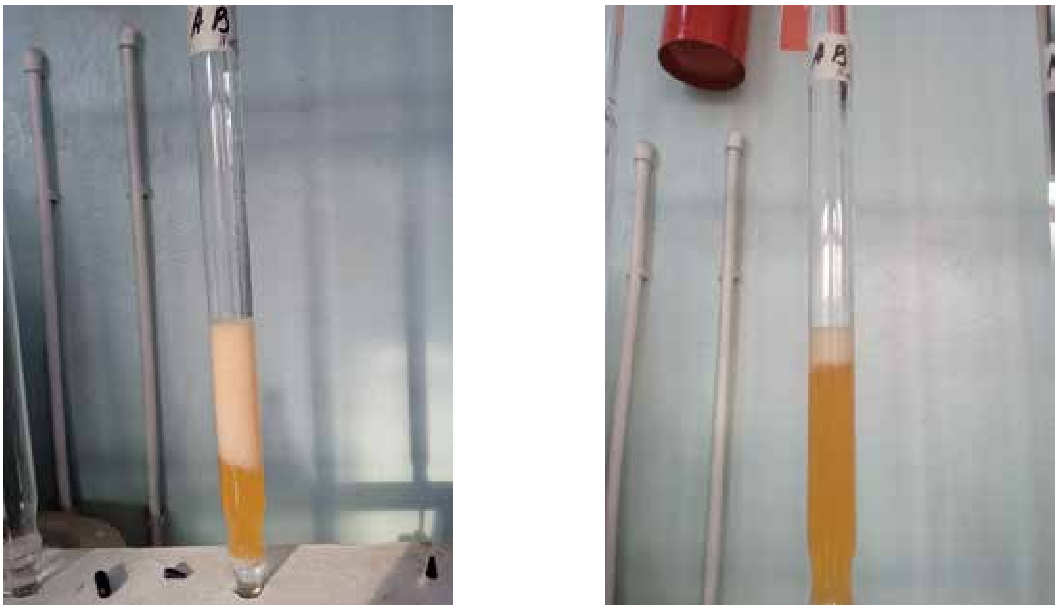
Table 8. *General analytical parameters of water samples before and after passing through KU-2/8 resin (KU 2 R, KU 3 R, KU 4 R)*

No.	Parameter	Results			
		Soda Workshop No. 3 Wastewater	KU 2 R	KU 3 R	KU 4 R
1.	Hydrogen ion concentration (pH)	7.86	1.81	2.16	2.02
2.	Magnesium ions (Mg^{2+}), mg eq/dm³	17.0	1.75	7.5	3.1
3.	Calcium ions (Ca^{2+}), mg eq/dm³	25.0	0.9	7.0	4.5
4.	Total hardness, mg eq/dm³	42.0	2.65	14.5	7.6
5.	Total alkalinity, mg eq/dm³	22.0	0.0	0.0	0.0
6.	Sodium ion mass concentration (Na^+), mg/dm³	0.13	0.07	116.6	133.9
7.	Potassium ion mass concentration (K^+), mg/dm³	16.3	3.7	12.8	10.7
8.	Chloride ion mass concentration (Cl^-), mg/dm³	31.9	26.5	24.8	26.5
9.	Nitrite ion mass concentration (NO_2^-), mg/dm³	0.0	0.4	0.3	0.66
10.	Nitrate ion mass concentration (NO_3^-), mg/dm³	56.0	0.2	0.0	0.0
11.	Ammonium ion mass concentration (NH_4^+), mg/dm³	0.0	0.0	0.0	0.0
12.	Iron (Fe^{3+}) ion mass concentration, mg/dm³	0.06	0.037	0.063	0.063
13.	Sulfate ion mass concentration (SO_4^{2-}), mg/dm³	1152.0	814.0	887.4	887.4

Second Regeneration of AB-17/8 Anion-Exchange Resin

After the 2nd regeneration, the AB-17/8 anion-exchange resin changed color, and a sludge-like mass formed inside it. To reuse the resin, it needed to be washed until it reached a neutral state. The resin was washed with 7.5 liters of distilled water over a period of two weeks. However, the resin did not return to a neutral state and became unusable.

Figure 3. *Experimental Procedure*



The results showed that the KU-2/8 cation-exchange resin reduced total hardness from 42 mg eq/dm³ to 1.25 mg eq/dm³ in the first cycle and effectively removed Ca^{2+} and Mg^{2+} ions. The KU-2/8 resin remained effective for up to four cycles. The AB-17/8 anion-exchange resin efficiently removed SO_4^{2-} and NO_3^- ions, but underwent rapid degradation at high pH (Zhang, L., et al., 2021; Li, H., & Xu, Y., 2022; Kumar, A., et al., 2020; Chen, Y., et al., 2022).

In the FSD (mixed-bed) system, water passing through the KU-2/8 cation-exchange resin and then through the AB-17/8 anion-exchange resin reached a total hardness of 0.45 mg eq/dm³. At the same time, K^+ and NO_3^- ions were partially retained, maintaining the possibility of using the water as a liquid fertilizer.

Conclusion

KU-2/8 cation-exchange and AB-17/8 anion-exchange resins effectively reduced the hardness of RO wastewater. The mixed-bed (FSD) system decreased total hardness from 42 mg eq/dm³ to 0.45 mg eq/dm³, while partially preserving beneficial elements (K^+ and NO_3^-). The AB-17/8 anion-exchange resin degraded after strong alkaline regeneration. The FSD system also led to a sharp reduction in Ca^{2+}, Mg^{2+}, SO_4^{2-}, and NO_3^- ions. However, extensive demineralization highlighted the need to evaluate the water's suitability for use as a liquid fertilizer.

Reducing hardness is necessary to convert RO wastewater into liquid fertilizer, but excessive purification can reduce the content of beneficial elements. The study results indicate that the ion-exchange method effectively decreases the hardness of RO wastewater. For producing liquid fertilizer, it is important not to remove all ions, but to maintain an optimal balance, which requires the development of a technologically balanced approach.

The findings have significant scientific and practical importance for the environmentally safe recycling of RO wastewater and its utilization as a resource. Current and future studies are focused on implementing optimal strategies for converting RO wastewater into liquid fertilizer.

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