

Linking Two-Year Seasonal Variability in Karun River Water Quality to the Operational Performance and Fouling Behavior of a Full-Scale Reverse Osmosis System

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ABSTRACT

The quality of feed water has a major influence on the operation stability and fouling properties of reverse osmosis processes; however, the impact of long-term surface water composition fluctuations under real conditions is still underexplored. The current investigation addressed the effect of two years of seasonal surface water characteristics on membrane operation and fouling potential. For a period of 24 months, raw water samples were collected on a monthly basis, and physicochemical parameters (total dissolved solids (TDS), electrical conductivity, turbidity, pH, alkalinity, hardness, major ions, silica, silt density index (SDI)) were calculated in terms of seasonal averages. Simultaneously, RO operational performance was evaluated in terms of membrane pressure difference, normalized permeate flow, specific energy consumption, and salt rejection. Water quality showed clear seasonal variation, with highest concentrations of TDS, hardness, calcium, chloride, sulfate, turbidity, and SDI in second year summer. SDI increased from 3.30 in the first-year winter to 6.05 in the second-year summer, indicating much more fouling potential. Consequently, the pressure difference in the membranes increased to about 180% of its original value, while permeate flow decreased to about 66% at the same time. The findings from correlation analysis show that SDI, TDS, hardness, calcium and sulfate are the most significantly correlated variables with the deterioration of RO performance. The results indicate the direct impact of seasonal variations in the source water quality on the degree of membrane fouling and hydraulic performance deterioration. Therefore, it is essential to continuously monitor the feed water and develop flexible management approaches accordingly, thus ensuring the stable performance and sustainability of RO systems.

Keywords: Karun River; reverse osmosis; feed water quality; membrane fouling; SDI; mineral scaling; long-term monitoring

1. INTRODUCTION

Freshwater is a basically indispensable natural resource that supports human wellbeing, economic progress, food security, and ecosystem sustainability, kind of all at once[1]. Even though water makes up about 71% of the Earth surface, only a small fraction is actually available in a form that humans can access, use, and keep using[2]. Meanwhile rapid population growth, industrialization, agricultural sprawl and climate change have raised the demand for high-quality freshwater, but also at the same time they put stronger strain on the water

resources that are already there[3]. So, maintaining water quality is now almost as important as securing water availability, because when water quality declines it can limit how the water is used, it pushes treatment costs up, it can lower treatment efficiency, and it creates serious environmental and socioeconomic problems[4]. River systems are another important source of freshwater on Earth and a very dynamic ecosystem, because their physical and chemical characteristics are governed by very complex interactions. There are several factors that affect the composition of river water, such as lithology, precipitation, the flow of rivers, surface runoff, groundwater, evapotranspiration, and land-use types influencing the physical and chemical properties of the river water[4, 5]. These interacting factors end up producing pretty big temporal, and seasonal swings in dissolved ions suspended solids and organic matter. In stretches where river discharge drops off, the water's dilution ability decreases, so you get higher concentrations of dissolved constituents[6]. On the other hand, when intense rainfall comes through, or there's flooding, the transport really ramps up—sediments colloids nutrients, and also contaminants get carried into the river systems more effectively[7, 8].

Climate change keeps on intensifying these processes a lot, by shifting precipitation patterns, driving droughts and floods more often, and changing hydrological regimes[9]. In turn those shifts mess with how pollutants get moved around, how well waters can dilute them, how sediments get mobilized, and also how geochemical reactions play out, until river-water quality is altered across a bunch of different time spans[10]. So long term monitoring programs really matter, because they help spot water-quality trends, explain which environmental factors are behind them, refine our ability to forecast what might happen, and back sustainable management of surface-water resources[8, 10]. The importance of seasonal shifts in water quality gets even more obvious when river water is used as feed water, for industrial treatment facilities[11]. In those circumstances, the changes in hydrochemical traits end up affecting pretreatment efficiency right away, membrane fouling too, plus the operational reliability of the whole system energy use, how often things need maintenance and even the total treatment cost[12]. So, grasping how the quality of the source water varies over time is key, not only for watershed management, but also for tuning the long-term performance of industrial water-treatment systems[13]. The Karun River is, basically, the biggest perennial river in Iran and it counts as one of the most important freshwater assets for municipal supply, farming, hydropower generation, and also industrial development[14]. It runs from the Zagros Mountains across the Khuzestan Plain, then it finally discharges into the Persian Gulf, but along the way it shows big spatial and seasonal shifts in water chemistry[15]. This happens because of different geological formations, hydrological fluctuations, climate conditions, agricultural return flows, industrial operations, urban wastewater discharge, and even land-use change[16]. All those natural along with human driven influences end up shaping the river's physicochemical properties quite a lot, and as a result they steer the water quality that gets delivered downstream for users[17, 18]. Previous investigations have documented some noticeable temporal shifts in the hydrochemical characteristics of the Karun River[19]. Naddafi et al. described long-term patterns in major water-quality parameters and really highlighted the need for ongoing monitoring, for assessing environmental variations and helping with water-resource management[17]. Dadolahi-Sohrab et al. showed that water quality tends to worsen during dry periods because the river discharge drops, and the concentrations of dissolved constituents go up[20]. In addition, Jahangiry Fard et al. pointed out that evaporite formations in the Gotvand region are an important geological source, giving rise to higher salinity and a modified ionic composition within the river[21]. Taken together, these studies suggest (or at least strongly indicate) that the hydrochemical characteristics of the Karun River are governed by the interplay between hydrological processes, geological setting, and also human activities. Since the Karun River is one of the major supplies of water for lots of industrial facilities, the seasonal swings in water chemistry, can really mess with how well treatment works and what it costs to run. Changes in dissolved solids, the substances that help create hardness, suspended sediments, organic material, and those scale forming ions can push pretreatment higher, speed up membrane clogging, lower overall process efficiency and steadiness, make energy use climb, and also mean maintenance shows up more often. In the end that means the total expense of water treatment goes up, quite a bit[21-23]. Reverse osmosis, RO, has become one of the most broadly used membrane approaches for producing high-quality water across industrial, municipal, and desalination contexts. Even though it has a strong ability for stripping away dissolved salts, inorganic contaminants, microorganisms, and plenty of organic compounds, stable RO operation really hinges on the feed-water quality. When the feed varies in physicochemical behavior, especially when dissolved solids rise, along with suspended particles, colloidal matter, natural organic matter, silica, calcium, and sulfate, the system sees quicker membrane fouling and scale formation. This then gives you lower permeate flux, more transmembrane pressure, greater specific energy use, more frequent chemical cleaning

cycles, and, in the long run, a shorter membrane life[24-26] . Membrane fouling is still, one of the big operational headaches that sort of restrain efficiency and long-term sustainability in RO systems. It can show up when stuff keeps piling on the membrane surface, like suspended particles, yes particulate fouling, but also colloidal materials and inorganic precipitates—often mineral scaling. Then you have organic compounds, and even microorganisms that manage to stick around. For RO systems fed by surface water, things get worse as turbidity rises, SDI goes up, and the concentration of scaling ions, such as calcium, sulfate and silica, is higher. In practice that combo substantially boosts the likelihood of fouling happening in the first place[24, 26, 27]. Consequently, it is quite important to monitor the feed water quality indicators together with the operational parameters, like SDI turbidity, the membrane pressure difference (ΔP), normalized permeate flow (NPF) and salt rejection. Also watch recovery rate and the cleaning-in-place (CIP) frequency, since this helps in evaluating membrane performance, and in developing more effective fouling control strategies[28, 29]. Even though a large number of research have explored either the hydrochemical characteristics of Karun River or the mechanisms of RO membrane fouling, only a few studies have quantitatively analyzed the relationship between long-term seasonal changes in the quality of river water on one side and performance of full-scale industrial RO system under real operating conditions on the other. Previous works related to Karun River basin research mainly concentrated on evaluation of water quality, soil water hydrochemical evolution and drivers[19, 24, 30] while research dedicated to membrane fouling was mainly aimed at studying fouling mechanisms in laboratories or evaluating performance of membranes separately from long-term environmental changes[27, 28]. Thus, until the present moment, the idea of how seasonal variation of raw water quality affects the performance of membranes under operational conditions has not been studied enough. In order to fill this gap in knowledge, the current study combines a two-year dataset of seasonal hydrochemical monitoring with the long-term operation data of a functioning RO plant that uses the Karun River for feed water. The influence of seasonal changes in the quality of feed water on fouling tendency and efficiency of membrane operation is studied in detail by evaluating a number of physicochemical parameters, such as silt density index (SDI), pressure difference (D.P.), normalized product flow (NPF), salt rejection, recovery rate and cleaning-in-place (CIP) effectiveness. The fusion of a wide range of knowledge opens up a new understanding of the connection between environmental variability at basin level and RO operation efficiency and gives some advice about how to apply best practices in monitoring, fouling control and sustainable operation of RO technologies using surface water.

2. Materials and Methods

2.1. Sampling, Transportation, and Preservation of Water Samples

To study the changes in water quality in the Karun River over time, water samples were taken once a month from the point of entry of water into the reverse osmosis (RO) plant. This was done as part of a two-year research program where several water samples were collected in the course of 24 consecutive months. Each time the sample was taken, roughly 20 liters of water was collected in an appropriate container and stored safely for testing[27, 31].

2.2. Physicochemical Characterization of Raw Water

The analytical methods outlined in Standard Methods for the Examination of Water and Wastewater (23rd Edition) [13] were used to assess the physicochemical properties of water from the Karun River. The variables determined were pH, turbidity, total dissolved solids (TDS), total hardness, calcium hardness, magnesium hardness, total alkalinity, acidity, hydroxide, carbonate, bicarbonate, chloride, phosphate, sulfate, total iron, manganese, and silica[31, 32]. Water pH was checked with a calibrated digital pH meter, while turbidity got measured by the nephelometric method. Electrical conductivity, or EC, was also recorded using a digital conductivity meter and the TDS values were kind of estimated automatically from EC with the conversion factor the manufacturer recommended, built right into the instrument. For total hardness and calcium hardness, they used the ethylenediaminetetraacetic acid, EDTA, titrimetric method[32]. Magnesium hardness is calculated by subtracting calcium hardness from total hardness. Total alkalis, acidity, hydroxides, carbonates, and bicarbonates content were measured using conventional acid-base titration method. Chloride was determined using argentometry, while phosphate, sulfate, iron, manganese, and silica contents were calculated using UV-Visible spectrophotometric method as per the standard methodology[32, 33]. They fouling potential in the raw water got evaluated with the Silt Density Index SDI, based on ASTM D4189-07 (Reapproved 2014) [14]. Basically, the raw water was pushed through a 47-mm membrane filter, with an

advertised pore size of $0.45 \mu\text{m}$, while keeping the filtration pressure steady at 30 psi. Then the SDI_{15} was worked out from the filtration times noted right at the start of the run, and again after 15 min of nonstop filtration, as required by the ASTM method [32, 34, 35].

The physicochemical parameters that were looked at in this study, along with the analytical methods and measurement instruments that were used, are set out in Table 1.

Table 1. Physicochemical parameters measured in raw water and analytical methods.

Parameter	Unit	Analytical Method	Instrument / Measurement Method
pH	–	SM 4500-H ⁺ B (Electrometric Method)	Digital pH Meter (Model: PHS-550)
Turbidity	NTU	SM 2130 B (Nephelometric Method)	Digital Turbidimeter (Model: TES-1386)
Total dissolved solids (TDS)	mg/L	Estimated from electrical conductivity (EC) using the manufacturer's conversion factor	Digital Conductivity Meter (Model: CON500)
Total hardness	mg/L as CaCO_3	SM 2340 C (EDTA titrimetric method)	EDTA titration
Calcium hardness	mg/L as CaCO_3	SM 3500-Ca B	EDTA titration
Magnesium hardness	mg/L as CaCO_3	Calculated as total hardness minus calcium hardness	Calculated value
Total alkalinity	mg/L as CaCO_3	SM 2320 B	Acid titration
Acidity	mg/L as CaCO_3	SM 2310 B	Titration
Hydroxide (OH^-)	mg/L as CaCO_3	SM 2320 B	Acid–base titration
Carbonate (CO_3^{2-})	mg/L as CaCO_3	SM 2320 B	Acid–base titration
Bicarbonate (HCO_3^-)	mg/L as CaCO_3	SM 2320 B	Acid–base titration
Chloride (Cl^-)	mg/L	SM 4500- Cl^- B (Argentometric Method)	Silver nitrate titration
Phosphate (PO_4^{3-})	mg/L	SM 4500-P E (Ascorbic Acid Method)	UV–Vis Spectrophotometer (Digital i3, Hanon, China)
Sulfate (SO_4^{2-})	mg/L	SM 4500- SO_4^{2-} E (Turbidimetric Method)	UV–Vis Spectrophotometer (Digital i3, Hanon, China)
Total iron (Fe)	mg/L	SM 3500-Fe B (Phenanthroline Method)	UV–Vis Spectrophotometer (Digital i3, Hanon, China)
Manganese (Mn)	mg/L	SM 3500-Mn B	UV–Vis Spectrophotometer (Digital i3, Hanon, China)
Silica (SiO_2)	mg/L	SM 4500- SiO_2 C (Molybdosilicate Method)	UV–Vis Spectrophotometer (Digital i3, Hanon, China)

2.3. Evaluation of Reverse Osmosis (RO) System Performance

The long-term operational performance of the reverse osmosis (RO) system was assessed through continuous operational data logged during the 24-month observation period. The performance indicators studied included pressure differential (ΔP), normalized permeate flow (NPF), salt rejection, permeate conductivity, feed pressure, recovery, and SEC. The data for operation design were collected from the monitoring system of the plant and daily records of operation and maintenance, making a long-term available dataset to examine the membrane work changes in time during real work conditions [24, 36].

To make it easier to compare operational parameters, when units and measurement ranges differ, all the performance indicators were normalized against the very first operating conditions. The readings taken

right at the start of monitoring, meaning Month 0, were treated like the reference points (baseline values) and were given a normalized value of one hundred percent. After that, each later measurement was turned into a percentage, meaning it was expressed relative to its matching baseline value, using the equation below:

$$\text{Normalized value (\%)} = \frac{X_i}{X_0} \times 100$$

where X_i is the value of the operational parameter measured at time i , and X_0 is the corresponding baseline value measured at the beginning of the monitoring period[37].

Normalization allowed direct compare of temporal trends among the operational indicators, even though their original units were different. it also made it easier to judge the progressive impacts of feed water quality fluctuations on RO system performance during the whole study period.

In order to enable comparisons of the various performance parameters characterized by different units and measurement systems, the normalized performance indicators were performed over time. At the same time, a comparison of the performance indicators with respect to their values relevant to the initial operating conditions was carried out. As for the dates of membrane chemical cleaning, they were included in the performance review to measure the performance of RO system after maintenance[28]

Spearman's rank correlation analysis was used to study the relationship between the feed-water quality and the performance of the reverse osmosis (RO) system. The correlation coefficients between the feed-water quality characteristics measured for total dissolved solids (TDS), silt density index (SDI), total hardness, calcium, sulfate, silica, and alkalinity, and the performance indicators of the RO system were calculated. Spearman's correlation makes it possible to assess the relationship because some of the variables did not satisfy the assumption of normality, thus this non-parametric method is suitable for the evaluation of monotonic relationships between two groups of data[38, 39]. Statistical significance was checked using a significance threshold, $P < 0.05$, and yeah it worked out. The resulting correlation coefficients were then shown as a correlation matrix, mostly to help with interpretation of how seasonal shifts in feed-water quality link up with the time-based changes in RO system performance, across the full two-year monitoring period.

2.4. Analysis of Temporal Variations in Water Quality

Statistical significance was looked at using a significance level of $P < 0.05$. The correlation coefficients that came out were put into a correlation matrix, so it would be easier to interpret how the seasonal changes in feed-water quality lined up with the temporal changes in RO system performance across the two-year monitoring period[39]. Along with the seasonal analysis, monthly shifts in a few selected water-quality parameters were put into time-series plots, so it was easier to see how things changed, both in the short run and over longer periods. This method, helped in giving a full look at the seasonal patterns, and also at the gradual, kind of progressive changes in the hydrochemical features of the Karun River across the whole two-year monitoring timeframe[40]. All data preprocessing, calculation of seasonal averages, and descriptive statistical analyses were carried out with Microsoft Excel 2021 (Microsoft Corp., Redmond, WA, USA). Statistical analyses, plus graphical visualization of temporal trends were done in XLSTAT (Addinsoft, Paris, France). Heatmaps, and correlation-matrix visualizations too, were generated using R software (version 4.3.2; R Foundation for Statistical Computing, Vienna, Austria) with the relevant packages for data visualization and hierarchical clustering. These visual results were used so that we could ease the interpretation of seasonal patterning, the interrelationships among water quality variables and how they relate to the RO system operational performance, overall.

3. Results

To look at temporal shifts in the hydrochemical traits of the Karun River, we took the monthly monitoring dataset that was collected over two back to back years and grouped it into seasonal averages. This way it was possible to judge both intra-annual, meaning seasonal variability, and interannual differences at the same time, while also reducing the effect of short-term disturbances. In the next sections we describe seasonal patterns in overall water quality parameters, the key ionic components, and hydrochemical indicators, then we discuss what those patterns imply for reverse osmosis (RO) system performance when operating at full-scale, and not just in a controlled or pilot setup.

3.1. Temporal Variations in General Water Quality Parameters

The outcome from monthly sampling, along with seasonal averaging, showed clear temporal and seasonal variability in the physicochemical characteristics of the Karun River over the course of the two-year monitoring period. Seasonal averages for the major water quality parameters are put together in Table 2, while the monthly variation trends are shown in Figure 1. In general, the changes that were noticed seemed to come from a mix of seasonal hydrological states, river discharge, evaporation, and this kind of surface runoff, too. In Figure 1A it looks like total dissolved solids, or TDS, and electrical conductivity, EC basically, show almost the same timing throughout the whole monitoring period. These two climbed to their highest levels during the summer seasons, and then they fell back down to their lowest values in spring. When river discharge was lower, and evaporation was more intense in summer, the dissolved salts got more concentrated inside the river water. That's why TDS and EC ended up higher. On the other hand, during spring river discharge picked up, so the dissolved constituents got diluted, and their concentrations dropped. This strong match between the seasonal trends of TDS and EC suggests, in a straightforward way, that electrical conductivity was mostly controlled by changes in dissolved ionic concentrations, and it also captured the seasonal shifts in river salinity.

The temporal variations in turbidity and the Silt Density Index (SDI) are shown in Figure 1B. In general, both parameters kept roughly the same seasonal shape, staying fairly low during winter and then rising stepwise from late spring into summer, yes. The peak values showed up in the second-year summer, when turbidity climbed to about 75 NTU and the SDI went up to 6.05. That seasonal lift likely comes from stronger surface runoff, more pronounced soil erosion, plus the movement of suspended sediment and colloidal particles into the river, especially when hydrological activity is more intense. The tight agreement between turbidity and SDI, basically tells us that when suspended solids went up, the particulate fouling potential of the feed water went up too. And because SDI is often treated as a practical metric for membrane fouling potential, these results imply that the RO system faced the highest risk of particulate fouling during the summer period, mainly in the second monitoring year.

In Figure 2, representative images of the SDI filter are given from seasonal average samples, and from visual inspection, clear seasonal differences in particle deposition can be seen. Filters that correspond to winter and spring samples show relatively little particle accumulation but those obtained during summer have much darker filter surfaces and more extensive particle accumulation. The filter that was obtained during the second summer of measurement had the highest deposition consistent with the highest SDI measured value of 6.05. The fact that the visual appearance of filters matches the quantitative SDI measurement indicates that the amount of particulates and fouling potential increased progressively in low-flow conditions.

While significant seasonal changes were evident in both dissolved solids and the suspended substance content, it should be noted that the pH remained consistent throughout the study period (see Figure 1C). The water in the river demonstrated the mildest alkalinity and pH that ranged between 8.32 and 8.76, which indicated minor changes in the acid-base properties due to seasonal variations of hydrologic regime, possible only to a limited extent. On the other hand, total alkalinity demonstrated moderate seasonal variability with significantly increased level during the summer and decreased one during spring. Indeed, these changes were related to the dissolved bicarbonate concentration variations caused by evaporation during periods of low river discharge and dilution during significant river discharge. Therefore, seasonal variation of water quality in the river was determined mostly by variations of the ionic composition and suspended matter rather than by strong shifts of pH levels.

It can be said that, according to the seasonal variation of the measured parameters, river discharge was the most significant factor affecting short-term changes of water quality in the Karun River. Parameters related to dissolved matter, such as TDS, EC, and alkalinity, were controlled mainly by dilution and evaporation, while turbidity and SDI were influenced mainly by flooding and resulting transportation of suspended particles. Thus, the hydrochemical patterns reflect the fact that the quality of raw feed water varies significantly throughout the year, which corresponds to the seasonal differences in membrane fouling characteristics.

Table 2. General parameters and main quality indicators of Karun River water (seasonal averages)

Season	pH	Turbidity (NTU)	TDS (mg/L)	Total Alkalinity (mg/L as CaCO ₃)	SDI ₁₅
First-year winter	8.46	18	886	184	3.30
First-year spring	8.32	19	788	172	3.95

First-year summer	8.69	53	1076	193	4.74
First-year autumn	8.54	24	924	182	3.48
Second-year winter	8.48	18	894	185	3.45
Second-year spring	8.38	61	798	173	4.25
Second-year summer	8.76	75	1090	195	6.05
Second-year autumn	8.60	27	936	183	3.82

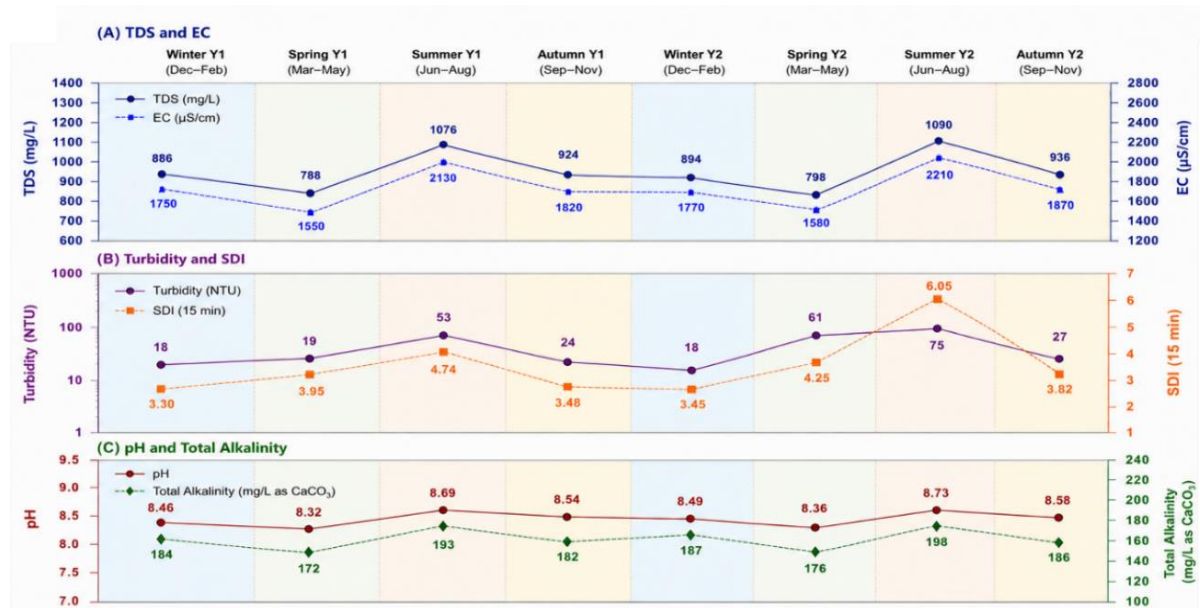


Figure 1. Seasonal trends of the physicochemical characteristics of raw water collected from the Lower Karun River intake over a 24-month monitoring period. Panel (A) presents TDS and electrical conductivity (EC), panel (B) shows turbidity and SDI15, and panel (C) illustrates pH and total alkalinity. Values represent seasonal averages for two consecutive monitoring years (Y1 and Y2). Background shading denotes the four meteorological seasons.



Figure 2. Representative SDI test filters obtained from the seasonal average raw water samples during the two-year monitoring period. The images are presented in chronological order from Winter (Year 1) to Autumn (Year 2). The visual differences in particle accumulation on the filter surfaces provide a qualitative indication of seasonal variations in the fouling potential of the feed water. Due to the large number of monthly SDI measurements, representative filters corresponding to seasonal average samples were selected for visual comparison.

3.2. Variations in Major Ions and Water Hardness

The seasonal variations of the significant ions dissolved and the other chemical substances are summarized in Table 3. As with the physical-chemical parameters, the concentrations of the main ions showed marked variations throughout the monitoring period. Such variations reveal mainly the components of river discharge, evaporation, geological erosion, and surface runoff. On the whole, the highest concentrations of ions were recorded in the summer, while the lowest concentrations were present during spring.

Overall hardness showed a gradual seasonal rise starting from about 200 mg/L as CaCO_3 in the spring of the first year until it reached a peak value of 236 mg/L in the summer of the second year. This increase could be mainly related to increasing calcium hardness, while seasonal fluctuations of magnesium hardness were not that significant. The high levels of calcium hardness indicate that hardness in the Karun River is largely determined by the dissolution of carbonate rocks. The more stable concentration of magnesium shows that minerals rich in magnesium are less important in terms of seasonal hardness changes of the water.

The concentration of chloride and sulfate showed similar trend to that of TDS, with the highest concentration during summer and the lowest during spring. Chloride concentrations rose from 227 mg/L in the first year during spring to 345 mg/L in the second year in summer. Sulfate concentrations rose from 69 mg/L to 85 mg/L from spring in the first year to summer in the second year. These seasonal rises are mainly due to evaporation during low-flow conditions, but there is also continuous supply from evaporitic geology in the basin of the Karun River. Strong correlation with TDS indicates that seasonal changes in salinity must have occurred due to the variation in the ionic concentration.

The behavior of iron was unlike that observed for the major dissolved ions as iron concentrations were found to be higher in spring when river discharge and surface runoff rates were increased. Such behavior can be attributed to erosion, which brings into the river small iron-containing particles from the surrounding soils. The concentration of manganese remained at low levels throughout the monitoring indicating that seasonal

variation in manganese is low. The concentration of silica varied only moderately and the data show that it was highest in summer, which indicates that there were no significant any weathering inputs during the study. Conducting the simultaneous evaluation of all the measured hydrochemical parameters demonstrated that the summer of the second year was the time when the raw water quality was at the worst levels. During that time, all the analyzed hydrochemical parameters like TDS, hardness, chloride, sulfur, turbidity, SDI, and silica reached their peaks at the same time. The water becomes very salty and with the high content of the suspended solids. The hydrochemical environment thus gained is considered to be favorable for the inorganic fouling and the particle fouling of reverse osmosis membranes. Therefore, the seasonal changes in the quality of the feed water are expected to influence the membrane performance and the effectiveness of the liquid separation. The study of these effects is carried out in the next section of the paper using data obtained from the long-term operation indicators of the full-scale RO system.

Table 3. Seasonal variations in the average concentrations of major ions and chemical parameters of Karun River water

Season	Total Hardness (mg/L as CaCO ₃)	Calcium Hardness (mg/L as CaCO ₃)	Magnesium Hardness (mg/L as CaCO ₃)	Chloride (mg/L)	Sulfate (mg/L)	Iron (mg/L)	Manganese (mg/L)	Silica (mg/L)
First-year winter	214	189	25	262	72	0.081	0.000	5.20
First-year spring	200	174	26	227	69	0.107	0.010	4.90
First-year summer	232	202	30	338	83	0.069	0.000	5.81
First-year autumn	220	194	26	281	75	0.080	0.000	5.10
Second-year winter	216	191	25	265	73	0.083	0.000	5.23
Second-year spring	202	176	26	231	70	0.110	0.010	4.95
Second-year summer	236	205	31	345	85	0.072	0.000	5.88
Second-year autumn	236	200	36	302	86	0.090	0.020	5.68

3.3. Reverse Osmosis System Performance

To figure out how seasonal shifts in feed water quality effect membrane behavior, the long-term operational side of the reverse osmosis system was examined using normalized performance indicators across the 24-month monitoring window. Normalizing, versus the starting operating conditions (Month 0 = 100%), made it easier to compare the various operational parameters even though they had different units and measurement scales. The time changes of the main performance indicators can be seen in Figures 3.

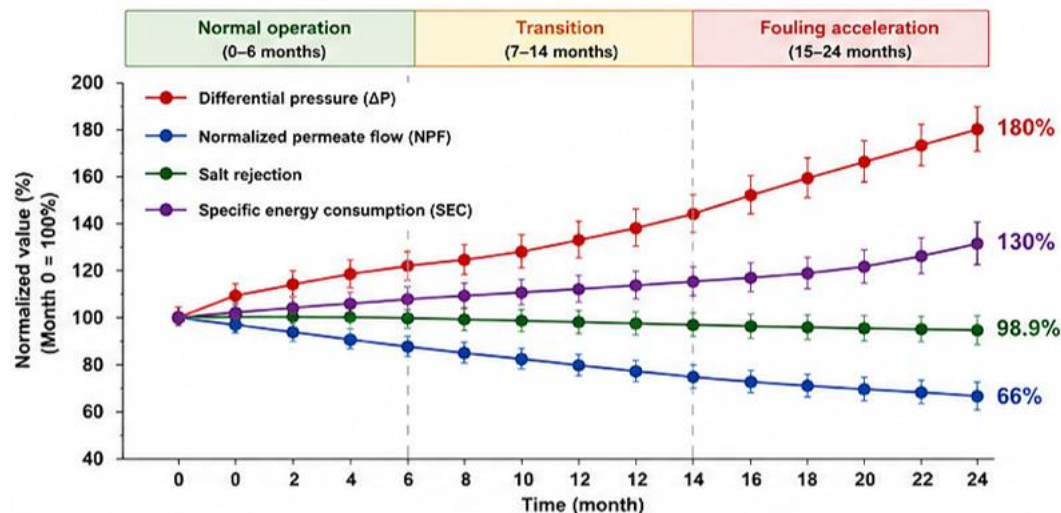


Figure 3. Temporal variations in the normalized operational performance indicators of the reverse osmosis (RO) system during the 24-month monitoring period. All operational parameters were normalized to their

initial values (Month 0 = 100%) to facilitate direct comparison among variables with different units and measurement scales. The monitored parameters include membrane pressure difference (ΔP), normalized permeate flow (NPF), specific energy consumption (SEC), and salt rejection. The shaded areas indicate the three operational phases defined for performance evaluation: Phase I (0–6 months), Phase II (7–14 months), and Phase III (15–24 months). Error bars represent the standard deviation of the measurements

As shown in Figure 3, all hydraulic performance indicators show a progressive kind of deterioration during the whole monitoring period, and its kind of keeps going. Membrane differential pressure (ΔP) increased continuously, it basically climbs up to about 180% of its initial value after 24 months of operation, and yes, it's not subtle. At the same time, normalized permeate flow (NPF) gradually drops down to around 66% of the baseline value, so overall it ends up reduced by nearly 34%. Then there is specific energy consumption (SEC), which rises steadily to roughly 130% of the initial value, meaning more and more energy input was needed to keep water production going as the hydraulic resistance keeps increasing. In contrast, salt rejection stayed quite stable across the monitoring period, about 98.9%, so even if the hydraulic side deteriorated a lot, the intrinsic separation efficiency of the membrane active layer stayed mostly unaffected

The simultaneous increase in differential pressure, decrease in permeate production, and rise in energy consumption are kind of hallmark signs of progressive membrane fouling. As particulate deposits and inorganic scale accumulated on the membrane surface, hydraulic resistance went up, which reduces water permeability while forcing higher operating pressure to keep system productivity going. The salt rejection staying fairly constant also points to the idea that the decline in performance came mainly from hydraulic fouling not from irreversible impairment of the selective membrane layer.

Through analysis of the operational data it is revealed that three phases of the process can be observed. During the beginning of operation (first six months), parameters remain stable, and only slight changes in term of pressure, permeate flow and energy usage occur. The second phase of the operation happens between the seventh and the fourteenth month when performance starts to deteriorate. Deterioration manifests itself in the increase in membrane pressure and feed pressure and decrease in normalized permeate flow. In the final phase of operation (months 15 to 24), deterioration process speeds up, and pressures reach the highest value while the lowest performance is recorded.

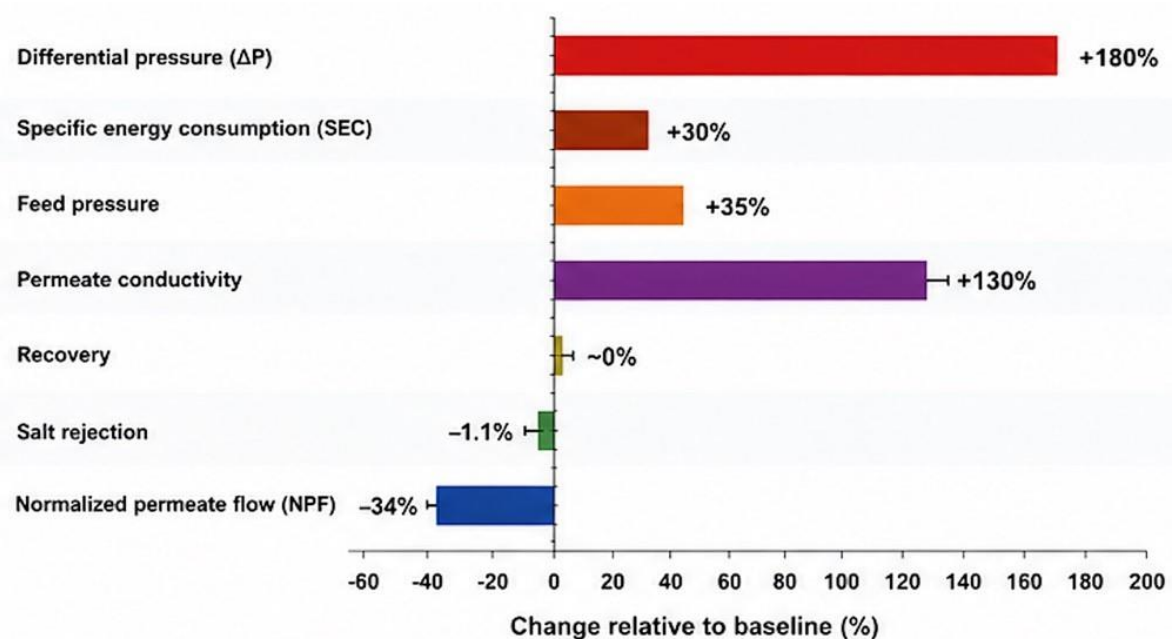


Figure 4. Relative changes in the operational performance indicators of the reverse osmosis (RO) system at

the end of the 24-month monitoring period compared with the initial operating conditions. Values are expressed as percentage changes relative to the baseline (Month 0). The evaluated parameters include membrane pressure difference (ΔP), normalized permeate flow (NPF), permeate electrical conductivity, feed pressure, specific energy consumption (SEC), salt rejection, and recovery

As indicated in Figure 4, the changes in the main operational parameters after two years of continuous operation are shown. Of the analyzed parameters, the membrane differential pressure showed the highest relative increase of about 180% in comparison with the baseline value. The conductivity of permeate also demonstrated significant increase, reaching about 130% of its initial value, which suggests gradual degradation of permeate quality in the course of long-term operation. The feed pressure and specific energy consumption increased by around 35% and 30%, respectively, while the normalized permeate flow dropped by about 34%. The recovery level has remained practically the same while the salt rejection decreased just by about 1.1%, which proves that the overall performance of membrane desalination was mainly preserved even though its hydraulic performance got worse.

The periodical changes of all the operational indicators were shown with a heat map presented in Figure 5. It could be seen from this figure that during the first months of operation all indicators remained in the appropriate range that confirmed that the membranes worked properly. Nevertheless, during the seventh month progressive deterioration of the performance indicators could be observed and this deterioration was particularly evident in the second year of operation especially in summer time that matched with the lowest quality of the feed-water being used for the process. Even though chemical cleaning (i.e. cleaning-in-place) led to the temporary decrease of the pressure difference over the membranes and some decrease of the normalized flow, still the effect was not that effective and the performance started deteriorating again immediately after the cleaning procedure. Thus, inability of the chemical cleaning to restore the initial operating conditions gives ground to the conclusion about the irreversible accumulation of fouling and scaling which cannot be removed by means of regular chemical cleaning methods.

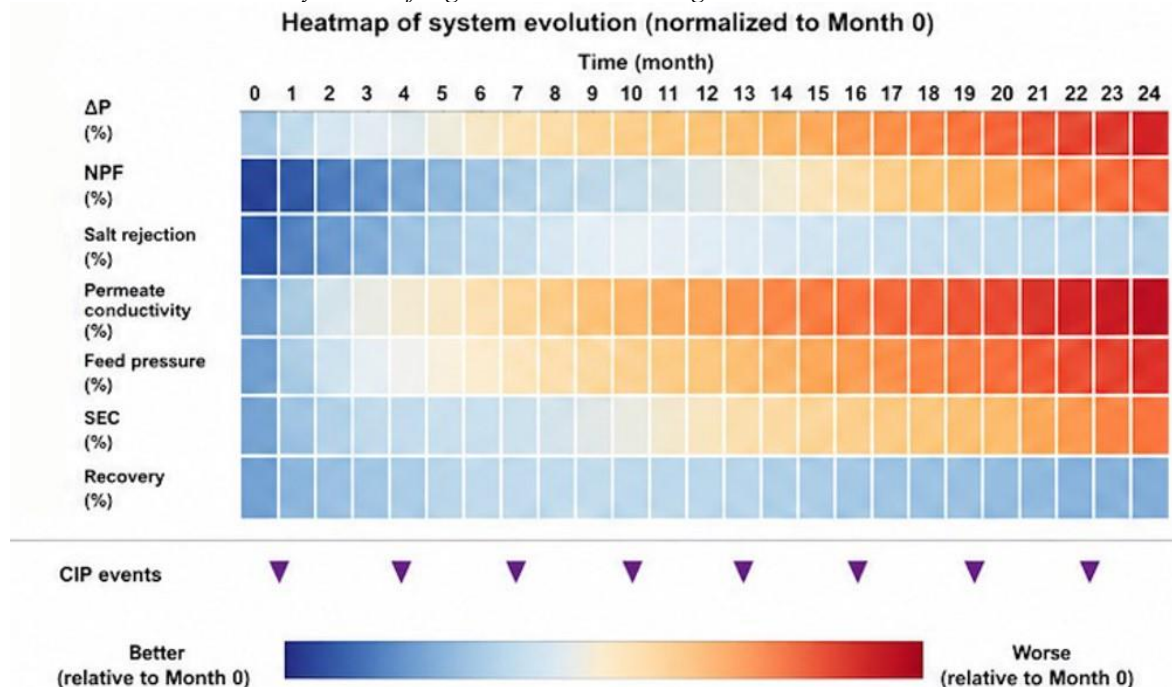


Figure 5. Heatmap illustrating the temporal evolution of the normalized operational performance indicators of the reverse osmosis (RO) system during the 24-month monitoring period. All operational parameters were normalized to their initial values (Month 0 = 100%) to facilitate comparison of temporal trends. Color intensity represents the relative magnitude of each parameter with respect to the baseline condition. Purple triangles indicate the timing of membrane chemical cleaning (cleaning-in-place; CIP) events.

To examine the connection between the quality of feed-water and the working of the membrane even more thoroughly, the values of the Spearman correlation coefficient were found as a link between hydrochemical characteristics and operational performance indicators (shown in Figure 6). The analysis of the obtained correlation matrix has shown that hydrochemical indicators, such as the total dissolved salts (TDS), silt density index (SDI), total hardness, calcium hardness, chloride, sulfate, and silica demonstrated strong correlation with differential pressure, feed pressure, permeate conductivity, and specific energy consumption, while having a negative correlation with the value of normalized permeate flow. It should be noted that TDS and SDI presented the strongest correlation with the decrease in performance which proves that dissolved solids and suspended solids have resulted in blocking the membranes even more. The results indicate simultaneous contribution of inorganic scaling and fouling processes to the deterioration of RO performance.

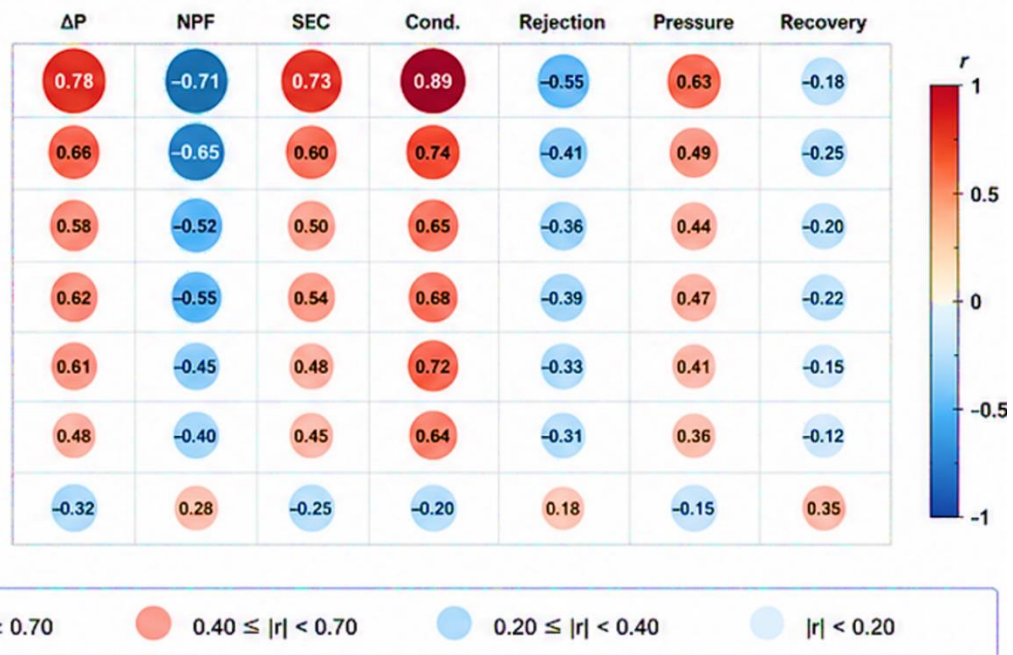


Figure 6. Bubble correlation matrix illustrating Spearman's rank correlation coefficients between feed-water quality parameters and the operational performance indicators of the reverse osmosis (RO) system during the 24-month monitoring period. Bubble color indicates the direction of the correlation (red, positive; blue, negative), whereas bubble size is proportional to the absolute value of the correlation coefficient ($|r|$). The analyzed operational indicators include membrane pressure difference (ΔP), normalized permeate flow (NPF), specific energy consumption (SEC), permeate electrical conductivity, salt rejection, feed pressure, and recovery

In summary, based on the results of operations, it can be seen that there is a strong connection between the seasonal deterioration in feed-water quality, and the gradual decline in membrane effectiveness. Foul periods with high concentrations of dissolved solids, hardness, sulfate, chloride, turbidity, and SDI always correlate with high hydraulic resistance, high energy expenditure, low permeate flow, and progressive deterioration in the water quality. Still, the continually high rejection of salts, throughout the observation period, suggests that the deterioration of membranes has been hydraulic primarily, and not structural. This indicates that the seasonal hydrochemical variability of the water in the Karun River influences the efficiency and fouling of real industrial RO processes as well.

4. Discussion

The results of this study demonstrated that the water quality of the Karun River exhibited clear temporal and seasonal variations during the two-year monitoring period. Specifically, simultaneous increases in TDS, electrical conductivity, hardness, chloride, sulfate, turbidity, and SDI were mainly observed during summer, particularly in the second year. These variations indicate that the quality of water at the intake location reflects the interaction of climatic, hydrological, and anthropogenic processes at the watershed scale, as river water

quality is influenced by factors such as precipitation variability, runoff, evaporation, sediment transport, and human pressures[10, 41, 42].

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4.2. Role of Soil Erosion, Sediment Transport, and Colloidal Materials in Increasing Membrane Fouling Potential

One of the important findings of this study was the simultaneous increase in turbidity and SDI during periods of deteriorated raw water quality. The SDI value increased from 3.30 in the first-year winter to 6.05 in the second-year summer, indicating an increase in the fouling potential caused by suspended particles and colloidal materials in the feed water. Although soil erosion and sediment load were not directly measured in this study, the simultaneous increase in SDI, turbidity, and hydraulic performance deterioration suggests that the transport of fine suspended particles likely contributed to changes in feed water characteristics[44, 45].

In river basins, variations in precipitation, runoff, land use, and erosion can increase the transport of clay particles, particle-associated organic matter, and mineral compounds, thereby altering the physical and chemical characteristics of raw water[10, 46, 47]. Suspended and colloidal particles are among the major initiating factors of RO membrane fouling, and their accumulation can increase hydraulic resistance, raise pressure drop, and reduce permeate flux[44, 48].

In the present study, the increase in ΔP and decrease in NPF during the second half of the operation period occurred simultaneously with increased SDI values in the feed water. This trend indicates the probable role of increased suspended and colloidal particle loading in intensifying hydraulic fouling of the membrane. Therefore, long-term monitoring of indicators such as SDI and turbidity can be used as an effective tool for predicting fouling risks and optimizing RO system operation[24, 28, 49].

4.3. Effect of Changes in Ionic Composition and Mineral Scaling Potential on RO System Performance

In addition to suspended particles and colloidal materials, changes in dissolved feed water composition play an important role in the long-term stability of RO systems. The results of this study showed that increases in TDS, total hardness, calcium hardness, chloride, and sulfate mainly occurred during summer, particularly in the second year. These variations, concurrent with reduced river flow, indicate an increase in dissolved ion concentrations during low-water periods. Increased concentrations of scale-forming ions can enhance the potential for mineral scaling on membrane surfaces and consequently affect system hydraulic performance[49-51].

In RO systems, concentration of ions such as calcium, sulfate, carbonate, and silica at the membrane surface can create more favorable conditions for mineral scale formation. Although direct scaling indices such as LSI or membrane deposit composition were not evaluated in this study, the simultaneous increase in calcium hardness, sulfate, silica, and TDS indicates an increased scaling potential of the feed water[52, 53].

In the present study, the increase in total hardness from approximately 200 to 236 mg/L and sulfate from 69 to 85 mg/L occurred simultaneously with increases in ΔP and SEC. This temporal coincidence suggests that increased ionic loading in the feed water, together with particulate fouling, likely contributed to increased membrane hydraulic resistance. Furthermore, the increase in silica concentration from 4.90 to 5.88 mg/L may contribute to silicate scale formation or participate in the development of multi-component fouling layers[54].

The relatively stable salt rejection performance (approximately 98.9%) indicated that the decline in system performance was mainly associated with increased resistance to water transport due to fouling layer formation rather than severe damage to the active membrane layer. Similar behavior has been reported in recent studies investigating RO fouling development under long-term operating conditions[24, 52].

In addition to hydrological factors, geological characteristics of the Karun River basin may influence the ionic composition of the water. The presence of the Gachsaran evaporite formations, including gypsum and halite, can increase concentrations of ions such as sulfate, chloride, and calcium through dissolution processes. Previous studies conducted in the Karun River have also reported relationships between these formations and increased TDS and hydrochemical variations of river water[55].

Overall, the results indicate that increased ionic constituents in the Karun River alone may not be the primary cause of RO performance deterioration; however, when combined with increased SDI and suspended particle loading, they create more favorable conditions for the formation of multi-component fouling layers and long-term membrane performance decline.

4.4. Relationship Between Feed Water Quality Variations and RO System Performance Decline

Long-term monitoring of the RO system demonstrated that variations in raw water quality from the Karun River were accompanied by changes in system performance. The increase in ΔP , reduction in NPF, and increase in SEC throughout the operation period indicate increased membrane hydraulic resistance due to gradual accumulation of fouling materials. In contrast, the relatively stable salt rejection performance suggests that the active membrane layer did not experience significant damage during this period, and that performance decline was mainly related to increased resistance to water transport [52].

Correlation analysis showed that TDS, SDI, total hardness, calcium, and sulfate exhibited the strongest relationships with operational performance variations. This pattern suggests that RO performance deterioration likely resulted from the combined effects of particulate fouling caused by suspended and colloidal materials and increased mineral scaling potential associated with dissolved ions. Previous studies have also confirmed the critical role of feed water quality, particularly particulate-related indicators and scale-forming ions, in the long-term performance of RO membranes [24, 52].

Although periodic chemical cleaning (CIP) resulted in temporary improvements in some performance indicators, the overall decline in performance continued during the remaining monitoring period. This finding indicates that long-term fouling management requires not only operational measures but also continuous monitoring of feed water quality and consideration of variations in the water source [24, 56].

4.5. Management Implications and the Need for an Integrated Water Management Approach

The findings of this study demonstrate that changes in RO system performance are influenced not only by operational conditions but also by variations in feed water quality resulting from broader watershed-scale processes in the Karun River basin. Reduced flow, increased dissolved ion concentrations, sediment transport, and variations in suspended particle loads are among the factors that can modify the characteristics of water entering membrane systems and increase operational costs.

Therefore, improving the sustainability of RO systems requires an integrated approach involving optimization of pretreatment processes, continuous monitoring of indicators such as SDI and TDS, appropriate membrane cleaning management, and consideration of water resource protection and erosion control within the watershed. Within this framework, membrane fouling should be considered not merely as an operational challenge but as part of the continuum linking watershed environmental processes with the performance of water treatment systems.

Conclusion

In this study, the temporal variations in the water quality of the Karun River and their impact on the long-term performance of a reverse osmosis (RO) system were investigated over a 24-month monitoring period. The results demonstrated that feed water quality exhibited distinct seasonal variations, and low-flow periods, particularly during the second-year summer, were associated with simultaneous increases in TDS, hardness, chloride, sulfate, turbidity, and SDI values. These variations indicate an increase in the ionic and suspended particle loads of raw water due to reduced flow rates, increased concentration of dissolved constituents, and changes in sediment transport processes within the Karun River watershed.

The increase in SDI and turbidity indicated that variations in the source water quality can enhance particulate fouling potential in RO systems, while increases in hardness, calcium, sulfate, and silica create more favorable conditions for mineral scale formation. The simultaneous occurrence of these changes with increased membrane pressure drop, decreased normalized permeate flow, and increased specific energy consumption demonstrates the significant role of feed water quality in the gradual deterioration of the hydraulic performance of the system. However, the relatively stable salt rejection performance indicated that the performance decline was mainly associated with increased resistance to water transport caused by fouling layer formation, and that no significant damage to the active membrane layer occurred.

Overall, the findings of this study demonstrate that fouling management in RO systems should not be limited only to treatment plant operations; rather, it requires long-term monitoring of source water quality, control of fouling indicators, optimization of pretreatment processes, and consideration of watershed-scale processes affecting feed water characteristics.

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