

**Review Article**

Brine Recycling: Towards Membrane Processes as the Best Available Technology

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To cite this article:Djamel Ghernaout. Brine Recycling: Towards Membrane Processes as the Best Available Technology. *Applied Engineering*. Vol. 3, No. 2, 2019, pp. 71-84. doi: 10.11648/j.ae.20190302.11**Received:** June 11, 2019; **Accepted:** July 8, 2019; **Published:** July 24, 2019

Abstract: For supplying drinking water throughout the world, there has been a huge growth in the usage of desalination factories. Nevertheless, the formation of brine (concentrate) is a complete side of the working of the desalination factory and encounters serious ecological defiance due to its elevated salinity. Thus, a cost-effective and environmentally friendly concentrate handling equipment is needed before its appropriate elimination. Presently, many elimination choices comprising surface water discharge, deep well injection, and evaporation ponds have been employed. Nevertheless, such methods are unsustainable and their application is restricted by an elevated capital cost and exclusive usages. Different traditional techniques comprising physicochemical, oxidation and biological methods with changing degrees of organics elimination have been noted. These days, membrane-based techniques seem to be cost-effective tools for treating brine since they could recuperate worthy resources and generate clean water with elevated recuperation. This review contributes to discussing the actual techniques for brine handling, comprising elimination usages and treatment methods. The features of the concentrate in a matter of water nature and its effect on open water bodies are reviewed. This work presents emerging membrane processes like forward osmosis, membrane distillation, and electrodialysis that are encouraging for reducing brine quantities, in recuperating worthy metals and enhancement of water recuperation. This discussion as well focuses on the reality that integrated membrane processes are better for concentrate handling for metals recuperation jointly with water decontamination in wastewater treatment factories and could attain a zero liquid discharge.

Keywords: Brine Disposal, Seawater, Brackish Water, Membrane Processes, Water Treatment, Electrochemical Methods

1. Introduction

A sufficient freshwater supply is a universal defy since the freshwater resources are draining at a worrying average [1, 2]. More than one billion people have no access to potable water and around 2.3 billion people (41% of the world population) are suffering from water shortages [3]. To prevail over this defy, desalination of seawater and brackish water employing high-pressure membranes comprising reverse osmosis (RO) and nanofiltration (NF) technology is viewed as a vital solution throughout the last decades since they generate excellent water quality [4-8]. Desalination technologies divide feedwater into clean water and concentrate streams famous as brine [9]. The standard water recovery of seawater RO systems changes from 40% to 50%

[10] and brackish water RO desalination factories usually run at recoveries of 75% to 85% [11, 12]. The degree of water recovery changes due to the diverse sample features, trans-membrane pressure, and the membrane sort employed for the treatment [13]. Nevertheless, the suitable disposal/management of the brine constitutes a hard environmental defy to most desalination factories as they contain very concentrated salts, organics, and else pollutants [5, 14].

Classical disposal solutions for brine are surface water discharge, deep well injection, evaporation ponds and land application [15]. Recycling concentrate is crucial both from environmental and economic viewpoints, especially for inland cities. As an illustration, in Canberra (Australia), sustainable management of concentrate stays one of the

important environmental and economic hindrances to the RO-based advanced reclamation plant [16, 17]. Even if classical recycling techniques have been frequently employed in practice, the worry of the protected recycling of brine has been brought into focus recently to decrease the capacity long-term hazard to nature and health [14]. As an illustration, in Brisbane (Australia), the Bundamba Advanced Wastewater Treatment Plant that contributes purified recycled water is required to treat brine and monitor the concentration of nutrients and metal ions before its discharge to the Brisbane River [18]. Many investigations have assessed the ecological disaster of concentrate recycling on soil deterioration, groundwater qualities, and the aquatic medium [19, 20]. Really, the brine has a harmful impact on aquatic living organisms [21, 22]. Nevertheless, the ecological consequences linked to concentrate discharge have yet to be sufficiently taken into account by the implied governments [5].

Different classical treatment methods like coagulation, adsorption, oxidation, and biological operations have been examined for the treatment of the concentrate solution. As a rule, the conventional techniques have been employed to decrease the global organic matter (OM) tenor from the concentrate [23]. Taking into account the constitution of the concentrate solution, the treatment objectives for concentrate may change. As an illustration, transforming concentrate waste to an applicable resource employing a treatment procedure may reduce both costs and ecological effects. During the last years, the brine solution has been employed more and more as a source of water for industrial and irrigation uses. Investigations established that these waste streams carry on a collection of rare and precious metals and metalloids comprising rare earth metals (like cerium and scandium), precious metals (such as palladium, platinum and rhodium), radioactive metals (like radium and uranium) and alkaline metals (such as lithium (Li), magnesium (Mg), and potassium (K)) [24, 25]. In fact, these elements are essential in the electronic and electrical industries, rendering them some of the most worthy non-renewable resources for our present-day community. Furthermore, if unsuitably liberated into nature, such elements may as well provoke serious ecological deterioration due to their poisoning. From this point of view, membrane-based techniques are appropriate since they can extract such minerals from a complex solution simultaneously with water purification [5, 26].

This review aims to explore the features of the concentrate solution and examine the existing brine recycling choices. In addition, the classical techniques are deeply evaluated with a view to minimizing the ecological impact of the recycling of RO brines. The capacity of rising membrane methods like forward osmosis (FO), membrane distillation (MD), and electrodialysis (ED) for concentrate treatment together with resource and energy recovery are revised. The challenges for membrane processes for generating clean water and resource recovery are also presented.

2. Features of RO Brine

Brine is the very concentrated saline water acquired in the last stage of the desalination process [27]. It as well includes different pollutants comprising precious metals, nutrients (like ammonia (NH_3), nitrate and phosphorus), trace organic chemicals (such as endocrine disruptors, pesticides, personal care products, and pharmaceutical products), effluent OM (like partially degraded organics and dissolvable microbial products), and pathogens. The existence of these rising pollutants, especially trace organic chemicals, in concentrate solution is of crucial attention. This is due to the probability of the extensive presence for their deficient decrease over the wastewater treatment equipment [28]. Even if they are detected in minimum levels ($\mu\text{g/L}$ - ng/L) in a concentrate solution, their long-term exposure may possess dangerous environmental impacts, which are yet to be entirely known [5, 29].

The quantity of pollutants in concentrate may augment by 4-10 time in feedwater [30]; therefore, it has an extremely destructive effect on both physicochemical and environmental features of the receiving mediums. The features of concentrate are a function of the quality of the feedwater, and the kind of the desalination process, the quality of the permeate water, the pre-treatment technique and the cleaning procedures and chemicals employed [31]. Investigations observed that the chemicals employed, like acids, antiscalants, and biocides, possess an impact on the chemical equilibrium of the dissolved matter [32]. Therefore, concentrate changes not only for pollutants but it may as well be various in the features of the organic and inorganic matter from the chemicals employing before the RO phase [5]. Researchers [33] detected that the RO brine from a water reclamation plant in California had observable degrees of copper (Cu), manganese, mercury, and selenium. They as well detected the existence of alkalinity (520-1490 mg/L as CaCO_3), NH_3 (62-98 mg N/L), chloride (800-1000 mg/L), and sulfate (1000-1480 mg/L) in the concentrate solution. Scientists [34] established that the RO brine from livestock wastewater treatment carried on NH_3 , humic substances, nitrate, phosphate, and K. The concentration of phosphate in concentrate was as elevated as 40 mg/L where the feed phosphate concentration was 5 mg/L [35]. Gomes et al. [36] proved that the RO brines from textile finishing plants were distinguished by elevated degrees of chemical oxygen demand (COD; up to 15 285 mg/L). Subramani et al. [37] mentioned that the RO concentrate acquired from the treatment of produced water (clean water produced during oil and gas production) as well carries on elevated concentrations of silica (>250 mg/L) and total organic carbon (TOC; >60 mg/L). The features of RO concentrate from industrial sites may be distinct from that from municipal sites. As an illustration, mine polluted groundwater treatment sites included an elevated concentration of calcium (Ca; >1000 mg/L), metals, silica (>200 mg/L), and sulfate (>4500 mg/L) [38]. Randall et al. [39] observed that the conductivity level of concentrate from the mining industry was roughly equal to the

electrical conductivity (EC) levels of RO brine from desalination plants (22 000 mS/cm). The EC was as elevated as 23 mS/cm for the concentrate solution from municipal wastewater [40]. The EC of concentrate is elevated due to its elevated salt content [41]. Barium (Ba), Ca, silica and sulfate were as well detected in the concentrate produced from the desalination of brackish groundwater [38, 42]. The existence of an elevated concentration of these pollutants will conduct to the saturation limits of barium sulfate (BaSO_4), calcium carbonate (CaCO_3), and calcium sulfate (CaSO_4) being surpassed, that way limiting the feed water recovery of the RO process due to scaling. Pramanik et al. [5] listed in a long Table the features of concentrate, illustrating the change of the water quality of concentrate.

3. Present Concentrate Recycling Strategies/Choices

Owing to the fact that desalination techniques produce huge quantities of concentrate, many recycling choices for concentrate are presently employed [43]. As noted above, the

conventional concentrate recycling choices are surface water discharge, deep well injection, land application, evaporation ponds, and traditional crystallizers. Pramanik et al. [5] presented an outline of the present concentrate recycling choices in the form of Table 1. Recycling choices of brine are a function of the volume of brine, quality of brine, the physical or geographical location of the discharge point of the brine, availability of the receiving site, the permissibility of the choice, public acceptance, capital and operating costs, and the capacity for the plant to be developed. The cost of recycling is a crucial parameter that requires to be considered before selecting which solution is to be used. Researchers [44] mentioned that concentrate recycling cost was a huge handicap to the large usage of this technique. The cost frequently changed from 5% to 33% of the total cost of the methods following the features of the concentrate, the degree of treatment before recycling, and the volume of concentrate to be recycled and the choice of the recycling solution. The detailed brine management choices are defined in the next section.

Table 1. A precis of actual concentrate recycling choices [5].

Technique	Merits	Drawbacks	Economic Remarks	Technical Remarks
Surface water discharge	<ul style="list-style-type: none">• Can manage a huge volume• Elevated dilution rates in the water body, potential dilution and blending with power plant discharge• Applied for facilities of all sizes• Natural processes enhance degradation	<ul style="list-style-type: none">• Restricted natural assimilation capacities forming negative effects on the marine environment if exceeded• Dilution is a function of local hydrodynamic parameters• Ecological consequences due to the diversities in salinity and major ion imbalance among brine and ambient surface waters, conducting to a negative effect on aquatic life• Stringent regulations (e.g., the National Pollutant Discharge Elimination System)• Good knowledge, monitoring, and planning programs of receiving waters are necessitated• Maximum capacity difficult to estimate• Dependent on appropriate, isolated aquifer structure• Needs convenient geological formation and confined saline-water aquifer, and not realizable for areas of elevated seismic activity or near geological faults	Low economic cost	Easy operation
Deep well injection	<ul style="list-style-type: none">• Appropriate for inland facilities/viable for inland plants with small volumes of brine• No marine effect predicted• Can be cost-effective to work• Can be employed to recharge aquifers	<ul style="list-style-type: none">• Augments the salinity of the groundwater• Elevated establishment, maintenance and regulatory compliance costs• Possible aquifer pollution brine waste may require to be treated• Highly limited capacity• Great areas of land needed• Elimination of unusable salts required	Cost efficient only for larger volumes	—
Evaporation ponds	<ul style="list-style-type: none">• Convenient for inland and coastal facilities• Simple to construct and execute, and low maintenance• Economical if the land is inexpensive• Likely commercial salt exploitation• No marine effect anticipated• Little technological and managing efforts needed	<ul style="list-style-type: none">• Energy-intensive• Low productivity• Climate-dependent/only probable in a dry climate with elevated evaporation• Huge physical footprint• Necessitate the control of erosion, seepage, and wildlife management• Hazard of the underlying soil and groundwater contamination• Requires regular monitoring• Problems if they overflow	<ul style="list-style-type: none">• Possible recovery of salts• High capital and operating costs	<ul style="list-style-type: none">• Great extents of land• Easy operation• Probable pollution of groundwater
Land application	<ul style="list-style-type: none">• Can be employed to irrigate salt-tolerant species	<ul style="list-style-type: none">• Storage and distribution system required• Inappropriate for great quantities of concentrate	—	Probable pollution of

Technique	Merits	Drawbacks	Economic Remarks	Technical Remarks
Conventional crystallizers/ zero liquid discharge	<ul style="list-style-type: none"> • No marine effect anticipated • Relatively simple to apply and low costs • Can be used to recharge aquifers • Appropriate for inland plants with small volumes of brine 	<ul style="list-style-type: none"> • Probable pollution of soil and groundwater, thus augmenting the salinity of groundwater and underlying soil • Dependent on seasonal irrigation requirements and climate • Necessitates huge areas of land • Probable negative effect of chemicals and pollutants on plants • Spray jet costs • Storage and distribution system required • Costly, capital and energy intensive • Still not realizable on an industrial scale • Large carbon footprint • Elevated energy consumption • Production of dry solid waste precipitates • Existence of heavy metals and different dangerous products 	High capital and operating costs	<ul style="list-style-type: none"> • soil, and thus, crops
	<ul style="list-style-type: none"> • Recovery of salts and minerals • Can generate zero liquid discharge • No liquid waste elimination • Avoids a lengthy and tedious permitting process • Smaller environmental effect • No marine effect anticipated 			<ul style="list-style-type: none"> • Technology accessible • More enhancement required to decrease energy use

3.1. Surface Water Discharge

The concentrate discharge into a surface water body comprising the seas, lakes, rivers, and lagoons is one of the most frequent management practices, and this is the least expensive of the brine recycling techniques in practice today [45]. The cost of concentrate discharged to surface water comprises the transportation cost of concentrate from the plant to the surface water discharge outfall, construction and operation cost of the outfall and controlling the ecological impacts comprising water quality evaluation. Researchers [46, 47] observed that concentrate from coastal desalination factories was directly discharged to seawater. Nevertheless, the first worry about surface water discharge is the pollution of the receiving waters. As a result, many mitigation measures such as the use of diffusers, blending and mixing zones may be adopted before discharge. As an illustration, concentrates may be diluted with natural seawater or municipal wastewaters to decrease its salinity degree before discharge. Investigations established that there is a minimal undesirable effect by decreasing the concentrations if rapid mixing and dilution are carefully employed in the discharge schemes [21, 44]. Researchers [48] mentioned that concentrate could be managed after blending with wastewater effluent or power plant cooling water. Squire et al. [49] defined how the concentrate is mixed with settled backwash water before discharge into surface water in the UK. [5].

3.2. Deep Well Injection

Deep well injection signifies the injection of concentrate into a deep aquifer under the groundwater layers [5]. The fundamental strategy of this technique is the capacity to prohibit motion of wastes into underground sources of potable water, the receiving aquifer must have the potential to capture concentrate formed during the plant life, and it must be hydraulically isolated from other aquifers. It should also be mentioned that if the concentrate does not carry on monovalent cations and heavy metals, this technology is the most interesting choice since it could evade precipitation of them before elimination. This method is usually employed for

the recycling of industrial, municipal and liquid hazardous wastes, and it is a function of possessing appropriate geological situations [50]. Before building an injection well, identified geological variables, as the depth and location of an appropriate porous aquifer reservoir, require being evaluated [51]. The capital cost for deep well injection is bigger than that of other disposal solutions. This choice possesses many challenges, which comprise choosing a convenient well site, corrosion and subsequent leakage in the well casing that may imply pollution of groundwater [51]. Consequently, this solution is only followed in the absence of another applicable choice.

3.3. Land Application

The land application may supply beneficial reuse of water if the concentrate is used in vegetation like for irrigation of lawns, parks, or golf courses. This technique may furnish a useful usage if nutrients may be needed. The choice of this solution is a function of many parameters comprising the availability and cost of land, cost of dilution water, the installation costs of the irrigation system, percolation rates, irrigation requirements, the salinity tolerance of the target vegetation, and meeting the groundwater quality criteria [48]. Following the Food and Agriculture Organization of the United Nations (FAO) [52], the allowable concentration of Ca, Mg and sodium (Na) ions for irrigation for general crops are 400, 60 and 900 mg/L, respectively. Nevertheless, there is a negative impact of land disposal of concentrate on soil and groundwater. Yoon et al. [34] suggested the reuse of concentrate from livestock wastewater as a low concentration liquid fertilizer in agriculture. Nevertheless, the reuse was only recommended if the sample did not carry on any pathogens. Mohamed et al. [19] observed that if concentrate was directly disposed into the permeable soil with low clay content and OM content, it had an undesirable influence on the underground aquifers. The high degree of salinity decreased soil permeability and decreased crop yield. As an illustration, Poon [53] mentioned that the EC should not override 1000 $\mu\text{S}/\text{cm}$ for long-term usage of a range of irrigated plants like cabbages, eggplants, and tomatoes [5].

3.4. Evaporation Pond

Evaporation ponds have been largely employed for concentrate recycling in several arid and semi-arid areas due to good the source of solar energy [31]. When water evaporates upon solar energy from concentrate, it conducts to the accumulation of precipitated salts [5]. This method is very easy and undemanding and comparatively effortless to build and needs low maintenance and little operator attention compared to mechanical devices. In this method, a series of ponds are built to ensure uninterrupted brine elimination. This technique requires to be realized as per the design and maintained and run duly so the ecological worries may be diminished, particularly the control of groundwater contamination [31]. This technique has been used in many countries comprising Australia, the Middle East, and the USA. Mickley [54] mentioned that around 6% of the desalination plants in the USA were employing this technology for concentrate removal up to 1993 and only 2% were using it after 1993. The decrease was mostly due to the augmentation in land price since this method needs a huge land area. Parameters related to this method are the evaporation rate, which is a function of the weather situations, mostly humidity, and temperature. The size of an evaporation pond is a function of the evaporation rates in the region, brine flow rate, surge capacity, freeboard, and storage capacity.

3.5. Conventional Crystallizers

Reclamation of metals from concentrate presents an interesting choice to evade removal problems, and it may give a supplementary economic advantage. As a result, treating brine for resource reclamation is a crucial defy for the researchers and industrials. A dual goal will be obtained if a rare and worthy component is extracted from concentrate that could decrease the ecological effect of RO brine elimination projects that would, first, enhance the economy of the treatment method [5].

A brine crystallizer technique is employed in the final phase of brine recycling devices. Nevertheless, this method remains costly if compared with evaporation pond, salinity gradient solar pond and deep well injection methods for brine treatment [55]. Mickley [46] observed that the crystallizer technology would be a more realizable choice if the building price of evaporation ponds is elevated, solar evaporation rates are low, and deep well injection treatment is costly. The concentrate discharge from a seawater RO plant in some places is mixed with seawater, and this stream is fed to a series of evaporation ponds, and after that to a salt processing factory [56]. Researchers [57, 58] assessed the evaporation and crystallization stages needed to regain salts from RO concentrate, and they employed lime softening in several steps of the evaporation–crystallization processes. They detected magnesium hydroxide ($Mg(OH)_2$) with a purity of 51-58%, calcites with a purity of 95% and $CaSO_4$ with a purity of 92%, after lime soda treatment. Seigworth et al. [59] noted that the integration of RO with evaporation and crystallization could attain zero liquid discharge. Therefore,

salts reclamation employing these techniques is viewed as being an applicable solution, even if more research remains needed to evaluate the economic parameters of salt generation. Ahmed et al. [60] estimated the applicability of reclaiming salts from RO brines from a desalination factory and they employed the patented SAL-PROC (Geo-Processors Inc., USA) techniques for sequential extraction of salts in the form of a crystalline, slurry, and liquid. They observed that the potential recovery products were a gypsum– $Mg(OH)_2$ (mixture), $Mg(OH)_2$, sodium chloride (NaCl), $CaCO_3$, sodium sulfate (Na_2SO_4) and calcium chloride, which establishes the potential cost-effectiveness of the desalination methods. Another research [61] illustrated that 45 million tons of salts are formed annually in the USA and around 70% of these salts were employed by chemical industries [5].

This section has discussed the solutions presently applicable and employed in controlling concentrate solution without more treatment. The next section of this work will show the traditional treatment techniques, which are mostly employed for the elimination of OMs. Since concentrate carries on a huge quantity of inorganic salts, many of the rising technologies that are employed to deal with concentrate simultaneously with the reclamation of salt and water are also reviewed.

4. Handling Brine Employing Traditional Treatment Techniques

The existence of pollutants in concentrate is of great worry since they may constitute dangers in nature [5]. Thus, eliminating them before protected removal in open water bodies or advantageous employment of recovered brine solution is necessitated. Different traditional treatment projects have been employed for dealing with concentrate, comprising chemical precipitation, coagulation, oxidation, and biological processes, either alone or in integration. It is sure that these techniques, omitting chemical precipitation, were mostly employed for OM elimination from brine.

4.1. Chemical Precipitation Method

Chemical softening has been largely employed for dealing with RO brine using lime softeners. The advantage of employing the chemical softening method for treating brine is the elevated elimination of scale-forming ions [5]. Nevertheless, the barrier of this technique is the formation of sludge that requires additional attention for suitable management. Scientist [62] employed the lime treatment to eliminate silica from RO brine and proved that this technique realized silica content elimination of 53-76%. Researchers [63] established that lime treatment was very efficient in eliminating silica from elevated silica RO brine and observed that no silica elimination happened until the lime injection surpassed the lime equivalent of the alkalinity. Another investigation [42] focused on the impact of lime softening for brine treatment from an inland RO plant at El Paso, Texas, USA and noted that up to 90% water recovery was reached

employing lime softening after decreasing the quantities of silica and BaSO_4 . Scientists [64] proved that the Ca tenor was eliminated as CaCO_3 after elimination of silica and metals (such as Ba) by coprecipitation with $\text{Mg}(\text{OH})_2$. When alkalinity was not present, sodium bicarbonate was injected to the RO brine for precipitating the Ca as CaCO_3 [65].

4.2. Chemical coagulation

Coagulation is an easy physicochemical and frequently used method for OM elimination from both water and wastewater [5, 66]. The pathways implicated during coagulation are charge neutralization and adsorption of OM on the metal hydroxide [67-69]. The performance of OM removal decrease is a function of the features of the polluted water, and the kind and dosage of coagulant employed [70, 71].

Coagulation has not experimented largely for application in concentrate treatment [5]. This is because concentrate carries on an importantly elevated tenor of salts. Following the simplicity of the method, this technique has been tested for eliminating the organic compound from an elevated salinity concentrate solution. Umar et al. [72] examined coagulation employing two aluminium-based [alum and aluminium chlorohydrate (ACH)] and two ferric-based coagulants [ferric chloride (FeCl_3) and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$)] for treating elevated salinity brine (EC of 23 mS/cm), and observed that at 1 mM dosage the dissolved organic carbon (DOC) reduction for the two ferric-based coagulants was comparable (40-43%) while that for ACH was astonishingly smaller (14%) than for alum (23%) injection. Dialynas et al. [73] examined the efficiency of alum and FeCl_3 coagulation for the brine received from a RO plant and discovered that the DOC decrease was 42% for alum (initial DOC, 8.5 mg/L) and 52% for FeCl_3 (initial DOC, 12.3 mg/L), with an optimum dosage of 2 mM as Al^{3+} and 0.4 mM as Fe^{3+} , respectively. This proved that iron-based coagulants seem to be more performant than aluminium-based ones for concentrate treatment. Employing a bigger concentration of FeCl_3 (1 mM Fe^{3+}) compared to Dialynas et al. [73] an importantly smaller elimination of DOC of 26.4% (initial concentration, 18 mg/L) from concentrate was mentioned by Zhou et al. [74].

Pramanik et al. [5] concluded that the lower removal of both DOC and COD was attributed to the existence of a considerable fraction of low to medium molecular weight (MW) compounds [42] in the concentrate. This was explained by the fact that coagulation procedure was unable to eliminate dissolvable OM with a low MW as it could mostly reduce high MW organics [75].

4.2. Electrochemical Coagulation

Electrochemical coagulation (electrocoagulation) is an efficacious technique for the treatment of elevated salinity water since it assures an outstanding EC that could decrease energy consumption [5, 76]. This method comprises an electrolytic recipient, with electrodes (aluminum or iron), in which polluted water is passed, and coagulation/flocculation happens with the metal dissolved from the electrodes [77]. The metal anode dissolution is produced simultaneously with

hydrogen gas bubble formation at the cathode, conducting to the fixation of the flocs and this then produces flotation of the suspended solids, lastly eliminating the pollutants [78]. The benefits of this electrochemical technology comprise less sludge formation if compared with a traditional coagulation method [79]. The defy of this technique is the elevated operation and maintenance costs linked with electrode change, elevated energy consumption, and restricted full-scale plant experience [80, 81]. Subramani et al. [37] examined the impact of electrocoagulation for the treatment of RO brine and mentioned that this process was very performant in eliminating Ba, Ca, Mg, strontium (Sr) and silica with more than 90% disposal. Other scientists [82] employed electrocoagulation as a pretreatment stage for the RO process for avoiding silica fouling and discovered that 80% of the silica was eliminated at a current intensity of 0.5 A and a hydraulic contact period of 30 min.

4.3. Oxidation-based Techniques and Biological Processes

Several oxidation-based techniques, like ozonation and $\text{UV}/\text{H}_2\text{O}_2$ application, and biological methods have been examined for brine recycling.

Ozonation has been largely employed for both water and wastewater treatment, especially for the decomposition and enhancement of biodegradability of the OM [74]. The OM is oxidized either via a direct reaction with molecular ozone (O_3) which is extremely selective or indirect reactions with free radicals ($\cdot\text{OH}$) [83, 84]. This technique has been announced for concentrate recycling either alone or in combination with additional treatments. Stand-alone O_3 was investigated for the decomposition of the organic tenor of brine solution by Lee et al. [85] and Zhang et al. [86] with identical initial COD and TOC concentrations for both samples of 60-65 mg/L and 18 mg/L, respectively. Zhou et al. [74] studied the impact of ozonation on the decomposition of OM from concentrate solution and observed the removal performances of DOC, COD and color were 22%, 14%, and 90%, respectively [5].

Following the infallible usage of $\text{UV}/\text{H}_2\text{O}_2$ technique for urban and industrial wastewater treatment, this method is earning attention for the treatment of concentrate solution [5]. Researches established that $\text{UV}/\text{H}_2\text{O}_2$ application is highly efficient in eliminating OM over a wide interval of MW. And the huge MW organics react faster than low MW chemicals, since the bigger organics are more aromatic in nature and contained higher molar absorptivities [87], therefore possessing a great number of reaction sites accessible to react with $\cdot\text{OH}$ [88].

The existence of elevated salinity in wastewaters is a serious problem touching the efficiency of biological methods. This is maybe due to an increased salinity concentration, which may generate off-balance osmotic stress through the microbial cell. In addition, therefore, this will produce the failure of the systems [89]. In addition, most of the organic chemicals existent in the concentrate solution are bio-refractory [74]; consequently, biological methods are seen unable for their elimination. Researchers [90] worked on the application of bioreactors for eliminating nutrients and

discovered that the existence of heavy metals like Cu and chromium in the feedwater block the efficiency of the nitrifying bacteria. Scientists [91] examined the biological nitrification-denitrification method for RO brine treatment.

More details about the above methods explored in this Section may be found in [5].

5. Resource Reclamation from Concentrate Employing the Adsorption Process

As seawater carries on several scarce and expensive metals, recuperating metals from the concentrate may be a motivating target for the water industry [5, 92]. Different kinds of adsorbents have been employed for mineral reclamation from seawater and brine [93]. Researchers [94] invented a protocol to extract precious elements from brine. They primarily precipitated the phosphates employing an alum blend of aluminum sulfate and iron sulfate. Afterward, they recuperated cesium (Cs) employing a liquid–liquid extraction technique via adding hydrochloric acid (HCl). Indium was recuperated with a purity of 97.4% by different liquid–liquid extraction with an organic phase constituted of three various acids. After that, they employed cation exchange resins for the extraction of rubidium (Rb; purity was not invoked) followed by germanium in the form of germanium dioxide with a purity of 99.8%. For the final step, they separated Mg, K, and NaCl following on their solubility phases.

6. Rising Membrane Processes for Brine Disposal: Water and Resource Reclamation

The application of the novel process for brine handling is actual demand, as most of the traditional techniques possess many drawbacks comprising expense and low productivity [95-97]. As a result, the capacity of varied rising membrane-based technologies like FO, MD, and ED for dealing with brine for generating cleaned water jointly with resource recuperation are debated in the following section. Recuperation of salts from brine can display the capacity for revenue formation and attains zero liquid targets [98, 99]. The United States Geological Survey Mineral Commodity Summaries [100] announced that around 21.7 million metric tons of salt were consumed nationally in 2010-2011. They mentioned that recuperation of salt from the desalination brine may decrease the deficiency of salt demand in the US and could contribute revenue of \$32 per ton from the rock salt in the brine [5].

6.1. Forward Osmosis

FO is one of the rising technologies that generates clean water by employing an osmotic pressure difference across the membrane as a driving force [101]. In this technique, an elevated concentrated draw solution is employed to form an

osmotic pressure difference across the membrane, and therefore water transport from the less concentrated feed stream to the elevated concentrated draw solution [102]. This method has been tested for various usages comprising wastewater treatment, saline water desalination, clean energy generation, and food processing [5]. A life cycle assessment study proved that integrating the FO method into conventional seawater desalination could decrease more than 25% of the ecological effect [103]. The main benefits of this process comprise low energy consumption as no external pressure is needed, the low fouling tendency with high water recovery compared to the pressure driven RO membrane filtration [15, 104, 105] and could be employed for feedwater with elevated concentrate. Researchers [106] observed that this method could attain more than 96% recovery throughout brackish RO brines treatment.

6.2. Membrane Distillation

MD is a membrane-based separation technique that employs a hydrophobic microporous membrane for separating the vapor phase from the feed stream [107, 108]. In this method, water is transported through the membrane and therefore MD can provide total rejection of all non-volatile constituents in the feed solution [5]. This technology can generate ultra-pure water at a lower cost compared to traditional distillation techniques [108]. MD processes are designed as vacuum, air gap, gas sweeping and direct contact. More information on MD could be found in the article by Pramanik et al. [25]. Considering the operating conditions for this process, the feed temperature has a crucial contribution in the permeate flux, followed by the feed flow rate and the partial pressure established on the permeate side.

The MD could be one of the future solutions for concentrate handling as it needs lower energy than traditional evaporation and could be coupled with a solar collector system, therefore minimizing the power consumption [5]. As an illustration, researchers [109] assessed that the thermal energy consumption was 2340 kW/m³ and 1609 kW/m³ without and with solar driven (photovoltaic panels), respectively, in a direct contact membrane distillation plant (DCMD) plant. A similar conclusion was obtained by other scientists [110] who announced that there was a 43% reduction in thermal energy consumption when a DCMD plant was run with 50 solar modules. Martinetti et al. [106] proved that the MD technique reached three concentration factors for seawater RO concentrate volume reduction. Tun and Groth [111] employed MD together with a crystallizer for the treatment of RO brine and reached feedwater recuperation of 95%. Janson et al. [112] employed a vacuum MD system to treat brine streams with a TDS of 100 000 mg/L and improved the feed water recovery. Ji et al. [113] tested the efficiency of a MD–crystallization process in terms of water recovery and NaCl crystallization kinetics and discovered that they could generate 21 kg/m production of NaCl crystals with 90% water recovery. Following the specific components of concentrate solution, especially worthy metals, this technique could be expanded for the recuperation of resources either in the feed stream or

permeate streams due to their unique transport mechanism. As an illustration, a non-volatile nutrient such as K and phosphate can be concentrated to enable nutrient precipitation. Researchers observed that NH_3 can be recuperated employing the MD process as NH_3 is more volatile than water and thus enriched their concentration in the permeate stream of MD processes [114, 115] and this can then be conveniently processed as a commercial fertilizer. Investigations observed that there was a greater NH_3 separation factor from urine in a vacuum MD (VMD) process where rejection of NH_3 reached to 99% [116, 117].

Nevertheless, the restriction of the MD process is scaling since salt could be precipitated on the membrane surface and this therefore participates to efficiency decay. Researchers observed that hydraulic membrane washing employing water could eliminate salt crystals from the membrane surface [118]. Martinetti et al. [119] studied the usage of vacuum-enhanced direct contact MD process for two different brackish water RO brines treatment with TDS concentrations of 7500 mg/L and 17 500 mg/L. They mentioned that water recuperations were higher than 98% for the first brine and 89% for the second brine. They also found that the membrane decreased the partial vapor pressure of water at higher feed concentrations, which could decrease the MD flux [119]. Similar to scaling, the OM could participate in the organic fouling of the MD membrane. They can clog the membrane pores, which conduct to a decrease of the membrane flux and oblige supplementary obstruction to heat and mass transfer, thereby decreasing the MD method productivity for similar usages [120]. Mericq et al. [118] examined the VMD to treat RO brine and obtained a total recuperation of 89% and noted that there was no organic fouling or biofouling after 8 h of procedure. Ji et al. [113] noted that the existence of organics in the RO brine could diminish the NaCl crystallization kinetics in terms of the decrease of the magma density, nucleation and growth rates [5].

6.3. Electrodialysis

Electrodialysis (ED) is an electrochemical separation method that employs electrical currents to eliminate salt ions selectively across a membrane, leaving clean water behind. The concept of ED operation is that the electrodes are connected to an outside source of direct current in a container of salt water. Throughout the ED procedure, all anions (chloride, sulfate, and nitrate) are accumulated in the acid chamber through the anode and all cations (Na and K) are accumulated in the base chamber through the cathode [5]. Following formation of acid and base, the treated water can be directly employed as product water. This technique can work with a continuous free chlorine residual of up to 1 mg/L [121], which allows better control of biofouling of the system. Following the feedwater quality, the water recuperation of this technology could be varied from 70% to 90%. Researchers observed that this technique was practical and lucrative for dealing with RO brine with a low to moderate salinity [86]. Zhang et al. [122] tested the ED method for desalinating RO brine with an EC ranging from 3.90 to 4.14 mS/cm and

established that 97.5% of feedwater recuperation was reached.

Electrodialysis reversal (EDR) is an identical method to ED. Reahl [121] tested the impact of the EDR system for RO concentrate treatment and attained 97% water recuperation. Medina et al. [123] observed that 92% water recuperation was realized employing EDR through the treatment of RO brine. He et al. [124] employed a pre-treatment system before the EDR for brine treatment and attained 96% feedwater recuperation. The Aquasel Desalination System [125] announced that if the concentration of Ca and sulfate ions in the concentrate is high, the brine sample from the EDR was transferred to a seeded crystallizer for precipitating gypsum for preventing scaling in the EDR system [5].

6.4. Membrane Capacitive Deionization (MCDI)

Capacitive deionization (CDI) is a desalination technique, which employs a capacitive electrode adsorption apparatus and electrical field as a driving force. The process is manipulated at low pressures and voltages for elimination of dissolved ions. In CDI techniques, the ions are eliminated when the electrolyte solution is transferred through a cell with a couple of electrodes. The detailed pathway of this method is explained elsewhere [126]. The ionic substances are attracted and adsorbed to the oppositely charged electrodes, and this conducts to deionized water formation. Nevertheless, the electrodes become saturated with ions after long-term usage and afterwards regeneration is needed through removing the electric field. The performance of the CDI process is a function of the surface area and adsorption features of the electrodes [127]. The CDI technique has a more elevated energy efficiency of salt elimination technology compared with the RO method. Nevertheless, the main restriction of this technique is its low recovery rate, and therefore it needed a more important number of expensive gel electrodes [5].

Researches proved that both adsorption and desorption happen altogether in this method, and so on decreasing the electrode potential as well as the current efficiency for ion removal. This issue may be conquered if the ion exchange membrane in front of the electrode could be employed in the CDI process. This technique is named membrane capacitive deionization (MCDI) [5].

6.5. Mixed Methods

Crossbred technique merges various methods to improve water recuperation of the desalination brine handling. Since such design joins many processes, it augments the desalination price 3–8 time following the geographical site and the enormity of the handling plant. Researchers [106] have noted that combining FO with the RO method gives a marvelously solid and multibarrier device for waste stream RO brines handling. Investigations established that combining the FO method with RO and MD can concentrate the diluted draw solution for the FO method, which can repeat the FO driving force jointly with increased quality clean water generation [128, 129]. On the other hand, the restriction of the

FO method is the gathering of pollutant in the draw solution. Scientists [130] noted that the pollutant passed out of FO process due to the incapable downstream RO or MD method, conducting to the build-up of the pollutant load in the draw solution. Researchers [131, 132] attained identical conclusion who observed that the huge collecting of OM in the draw solution was observed in an FO–RO combined device. As well, if the cumulative permeate volume augmented the collecting of microcontaminants in the draw solution augmented in an FO–MD mixed device [128, 129]. As a result, controlling this pollutant collecting in the draw solution is crucial to guarantee the sustainable efficiency of the mixed method [5].

7. Conclusions

The main points drawn from this work may be given as:

Desalination techniques are viewed as a vital means to prevail the restriction of water supply and augmenting request for water for both human uses and industrial applications for the future years. However, potential handling of the brine streams due to the hazardous and recalcitrant kind of several chemicals in the solution is a problem. Following the performance of the elimination of OM, traditional methods are supposedly considered as suitable processes thanks to their efficacious elimination and detoxification of OM. Elevated energy consumption for the oxidation method and sludge formation for the coagulation technique are serious hindrances to the application of these methods for such usages. In addition, the generation of by-product chemicals is an additional worry linked to oxidative processes. It is clear that the oxidative method would be an appropriate choice to enhance the biodegradability of concentrate solution making downstream biological treatment possible as it forms biodegradable organic chemicals. Nevertheless, the classical processes are exceedingly unavailing in eliminating other chemicals from the concentrate solution [5].

Membrane technology presents an efficacious option for concentrate handling, which may bypass the likely danger of employing frequent elimination choices and removal methods for concentrate treatment. This is explained by (i) most of the traditional removal solutions are inefficacious when taking into account the climatic parameters, geographical situations, and the environment, and (ii) traditional treatment techniques can only eliminate the OM. Therefore, they possess negative effects on both the aquatic medium and human beings, and environmentally friendly handling solutions are engineering defy. The benefit of concentrate is that it is composed of several worthy and scarce metals; thus, recuperating them may render a great benefit for the industry. The usage of emerging membrane-based techniques comprising MD, FO, and ED is interesting, reliable and environmentally friendly for concentrate disposal since they generate high-quality effluent with resource recuperation [133].

Jointly, the FO and MD methods could be employed in handling brine streams with increased TDS concentrations. The FO method needs lower energy consumption than other

treatment methods. An important benefit of both the FO and MD process resides in the existence of a waste heat source to heat the feed water to MD or restore the draw solution in FO. All these methods do not need applied pressure for concentrate treatments; nevertheless, the techniques are yet to be expanded at full-scale as most of the researches have been realized at laboratory or pilot scale.

As FO is an encouraging technique for brine handling, it is restricted by the osmotic pressure difference between the feed and draw solution. Thus, the extra enhancement of this technique is necessitated. As mentioned above, recuperating metals from concentrate is an encouraging choice, thus more investigation is required to expand selective extraction methods for the desired elements detected in concentrate [134]. Fouling is viewed as the principal barrier in membrane usages, which conducts to a decrease in its performance. As a result, fouling dominance design in the FO method is indispensable. Membrane fouling in the osmotic dilution technique may be diminished throughout using relatively easy monitoring designs that implicate hydrodynamic mixing. Improvements in the membrane material can elevate the membrane method performance concerning selectivity and flux, membrane durability, chemical resistance, pressure and temperature resistance, high packing density, and lower membrane cost. Improving membrane material will thus decrease the total cost linked to the usage of this technology. In addition, integrating various techniques may be applied in order to elevate the membrane flux efficiencies. Consequently, an FO/membrane bioreactor emerged with MD may be implemented to attain purified water with minerals' recuperation with a concept of zero liquid discharge [5].

Acknowledgements

The author wishes to acknowledge the authors of the [5] review paper, for their excellent work, which was widely cited in this review paper.

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