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Chapter

An Overview on the Treatment and Management of the Desalination Brine Solution

Reza Katal, Teo Ying Shen, Iman Jafari, Saeid Masudy-Panah, and Mohammad Hossein Davood Abadi Farahani

Abstract

Due to the increasing limitations of water resources, application of desalination plants is expanding. One of the constraints associated with desalination plant operation is the production of concentrated solution, which is known as brine and can lead to critical challenges in the environment due to its high level of salinity. In this regard, many different disposal options used recently to control and prevent the environmental issues may be caused by the brine. Evaporation ponds, surface water discharge, and deep well injection are considered as the most well-known options to properly dispose concentrated brine. However, the application of these methods is highly restricted by capital cost and their limited uses. The treatment methods vary in terms of their ability in organics removal and can be divided into three different conventional groups as biological, physicochemical, and oxidation. In recent years, more attention has been paid to membrane-based technologies due to their economic performance in recovering precious resources and providing potable water with high recovery rates. This book chapter provides some critical reviews on recent technologies including treatment operations and disposal options to manage concentrated solutions from desalination plants. Finally, electrodialysis, forward osmosis, and membrane distillation as emerging membrane processes are examined in this chapter.

Keywords: brine, management, treatment, disposal, metal recovery

1. Characteristics of brine solution

The by-product of seawater desalination is known as brine. Brine is extremely concentrated seawater that causes detrimental environmental impacts due to its high salinity and presence of multifarious contaminants. They include heavy metals, nutrients containing nitrogen and phosphorus [ammonia (NH₃), nitrate (NO₃⁻), and phosphorus (K)] derivatives, organic contaminants in minute concentrations (hormone and endocrinal disruptors, pharmaceutical and personal care products, soluble microbial products, and incompletely degraded organics found
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Table 1. 
Constituents of brine from various desalination plants [15].
in wastewater effluents), and pathogenic microorganisms. The identification of such trace organic contaminants is cardinal because it only serves to indicate the increased propensity of incomplete removal in most wastewater treatment systems across the globe [1]. Such prolonged exposure to such organic contaminants can lead to incomprehensible and detrimental impacts on our ecology albeit present in trace amounts. Environments in close proximity to brine discharge feedwater could be ravaged ecologically and physicochemically because the concentration of such contaminants is multiplied several-fold [2].

The matrix of brine depends on a confluence of factors—quality of water sources, desalination processes the brine is subjected to, the permeate water grade, pretreatment unit processes, and chemicals employed during the cleaning-in-place [3]. Research has shown that acids, antiscalants, and biocides have a direct consequential effect on the equilibria of the dissolved constituents [4]. As a result, the matrix of brine can differ because of the constituents’ concentration and characteristics due to the employment of chemicals during pre-RO treatment. Ersever et al. [5] found that the RO concentrate from a Californian water reclamation plant in California had trace copper (Cu), manganese (Mn), mercury (Hg), and selenium (Se) levels. Alkalinity presence was also identified in brine, ranging approximately from 500 to 1500 mg L\(^{-1}\) as CaCO\(_3\), alongside with NH\(_3\) at around 60–100 mg N L\(^{-1}\), chloride amounting to 800–1000 mg L\(^{-1}\), and sulfate at 1000–1500 mg L\(^{-1}\). Yoon et al. [6], on the other hand, found that the concentrate from the RO treatment of farm animals’ wastewater treatment contained NH\(_3\), humic substances, NO\(_3\)^{−}, phosphate (PO\(_4^{3−}\)), and potassium (K). PO\(_4^{3−}\) concentration reached up to 40 mg L\(^{-1}\) when the feed concentrations were as low as 5 mg L\(^{-1}\) [7]. Gomes et al. found that the concentrates from the RO treatment from textile plants had high levels of chemical oxygen demand (COD) of up to 15,000 mg L\(^{-1}\) [8]. Subramani et al. also noted that the RO brine obtained from treating water produced during oil and gas production contained high concentrations of silica and total organic carbon superseding 250 and 60 mg L\(^{-1}\), respectively [9].

The characteristics of RO brine from industrial areas, however, differ from municipalities. For example, groundwater treatment sites contaminated by mining activities contained high calcium, silica, and sulfate concentrations greater than 1000, 200, and 4500 mg L\(^{-1}\), respectively [10]. Randall et al. noted that the brine conductivity levels from mining industries were hovering at 22,000, almost on par to electrical conductivity (EC) levels of desalination plants’ RO concentrate [11]. Umar et al. posited that EC levels were almost at 25 mS cm\(^{-1}\) for brine solution from a municipal wastewater [12]. The high total dissolved solid (TDS) content is attributed to such high EC levels in brine [13]. Generation of brine from desalination of brackish groundwater was found to contain barium, calcium, silica, and sulfate [10, 14]. High concentration of these TDS causes scaling because the concentrations of barium sulfate (BaSO\(_4\)), calcium carbonate (CaCO\(_3\)), and calcium sulfate (CaSO\(_4\)) have saturated and exceeded their solubility limit (K\(_{sp}\)). This diminishes the permeate recovery of the RO process. The constituents of brine are shown in Table 1, which depicts the changes of the water quality. These variations occur because sources of influents are different, alongside with different design and operational parameters employed in the treatment processes.

### 2. Environmental impacts

Brine is defined as the waste by-product of desalination. A plethora of research studies have conducted environmental impact assessment studies of brine disposal on identified areas of concerns—marine, groundwater, and soil
environments [21, 22]. The environmental issues are as multifaceted as they are multifarious. Experts associate brine disposal with a correlated increase in salt concentrations of water bodies which are recipients of disposed brine. Brines with high TDS detrimentally affect the marine benthic communities living in close proximity to brine discharge. Brine disposal is also esthetically unpleasing. Moreover, the presence of chemicals used for pretreatment and membrane cleaning and corrosive metals are of pivotal concern. Salinity, temperature, and chemical composition of brine are reasons why brine poses a threat to our environments. The salinity and temperatures of brine depend entirely on the unit treatment processes employed. Brine salinity hovers at about 55–70 g/L, about 1.5–2 times much higher than seawater. Further, the brine produced by thermal-based technologies fluctuates at about 30–40°C, 1.37–1.82 times higher than seawater temperature at 22°C [23, 24].

The marine environments would not be harmed if brine was disposed from a sole desalination plant, but the collective discharge of brines from multiple plants operating close to each other for extended periods will. Numerous studies point to brine disposal as the core reason for osmotic balance disruption as it increases the salinity of marine life habitats. Living organisms will be deprived of water at a cellular level, and the increased salinity causes a turgor pressure decline [25, 26]. This may lead to the plausible eradication of species [27, 28]. Jenkins et al. propounded that several marine species could be detrimentally affected by salinity permutations of only 2–3 g/L, though some species may be sturdier to such salinity changes [29]. Petersen et al. also observed that a salt concentration increase of 10% above ambient levels destroyed both morphology and physiology of corals [30]. It was concluded that the dual confluence of increased salinity and polyphosphate addition (to reduce scaling and fouling in RO membrane) had a greater influence on all the sample sizes of corals tested.

There were exceptions where brine disposal had negligible impacts, which have been observed on the marine flora and fauna species [31]. These only occurred where abundant currents and choppy waters were present, i.e., Australia. Studies have also point to the alleviation of detrimental impacts brought about by brine disposal by suggesting the long-term use of multiport diffusers [32, 33].

Brine with temperatures higher than ambient seawater temperature by 10–12°C may have several harmful effects on marine fauna and flora. The toxicity effects brought about by metals and chemicals amplify significantly with temperature [34, 35]. Furthermore, various heavy metals like copper and nickel (found in alloys of heat exchangers) inadvertently become part of the brine stream when corrosion of heat exchangers occurs during desalination. In 2016, Alshahri investigated the concentrations of heavy metals in disposed brines of Persian Gulf desalination plants [36]. Sand and sediments near the Persian Gulf were found to contain copper, iron, and chromium, and their concentrations were higher than that in shale due to anthropogenic activities. Likewise, research on the Al-Khafji coastal sediments point to high levels of copper at the periphery of the coastline located north, plausibly due to brine disposal from nearby coastal desalination plants [37]. When evaporation ponds are unlined, the soil quality declines due to ionic replacements of calcium with sodium ions [21, 24], and underground aquifers are contaminated when brine is discarded in such areas [38, 39].

3. Common strategies for brine solution disposal

Large amount of brine is generated after the desalination process that many disposal options are implementing currently. According to previous sections, it has
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been mentioned that surface water discharge, deep well injection, land application, evaporation ponds, and conventional crystallizers are all considered as traditional methods for brine disposal. The quality and volume of the concentrate, as well as the physical and geographical locations of the output point of the concentrate, are the factors affecting the disposal options of concentrate. Also, to select an appropriate disposal option, it is necessary to consider the economic aspects, feasibility, general acceptance, authorization of the option, the availability of disposal site, and also the feasibility of facility development. One of the most important factors to be considered before selecting an option is the cost of brine disposal which is a barrier to the extended use of this process [40, 41]. Between 5 and 33% of the total cost of the process is usually related to brine disposal, and it depends on the features and volume of the brine, disposal option, and the level of brine treatment before being disposed. The details of different conventional brine disposal options are described in the following sections.

3.1 Surface water discharge

Discharging the brine directly to the open aquatic environment like lakes, rivers, bays, and oceans is considered as surface water discharge. The brine, after being transferred to a disposal site, sheds into the desired aqueous medium through a special structure. Most SW desalination plants are designed and perform based on this method (N90% of world SW plants). On the contrary, inland brackish water desalination plants are more limited based on that inland water bodies can be used as water sources because of their high quality. On this basis, the discharge can only be done when the composition of the brine is consistent with the receiving water body and suitable for discharging on that point [42, 43]. As previously mentioned, because of the higher-than-usual salinity of the brine or its ingredient pollutants that do not exist in the receiving water body, it can be detrimental to the marine environment. Appropriate restrictions and measures can make the brine disposal in surface water as a sustainable method for SW desalination plants [44]. For example, dilution of the brine using the municipal wastewater or regular SW before discharging to the marine environment is a kind of measure to decrease the salinity level of the discharging brine [45]. Research has shown that if dilution and rapid mixing are used with caution to decrease the concentration of the brine, it has a negligible adverse impact [46]. The cost range of this disposal method is from US$0.05 to US$0.30 based on 1 m$^3$ of brine rejected.

3.2 Discharge to the sewage system

A brine disposal method in which the brine is discharged into the nearby sewage collection system is called sewer discharge. Most of the small-scale BW desalination plants are using this method of discharge as the high TDS content available in the brine can potentially have a negative impact on the receiving wastewater treatment plant (WWTP) [47]. Generally, a high level of TDS content in influent which its concentration exceeds 3000 mg/L can inhibit the biological treatment process in a WWTP as the salinity is very high in this situation [48]. Given the concentration of SW brine TDS can exceed 55,000 mg/L, the daily capacity of WWTP must be at least 20 times higher than the volume of brine discharge in order to maintain the restricted range of influent TDS concentration lower than 3000 mg/L. Furthermore, a very high salinity of final wastewater effluent can have issues related to the environment and regulations during the final disposal process. In addition, the probable existence of heavy metal traces in the brine may require some measures like pH neutralization or other regulating procedures before
the main treatment process as a basic pretreatment. Such measures guarantee the substructure of the treatment process and also the quality of the final wastewater effluent [49]. Accordingly, sewer discharge is broadly used by BW desalination plants and is not consistent with SW desalination processes. The cost range of this disposal method is from US$0.32 to US$0.66 based on 1 m$^3$ of brine rejected [50].

3.3 Deep well injection

The procedure in which the brine is injected into a deep aquifer existing beneath the groundwater layers is called deep well injection. The most important matter must be considered before the injection is to ensure that wastes are not leaked to other locations, and the capacity of the target aquifer must be consistent with the plant life, and also this aquifer should be hydraulically isolated from surrounding porous media. This method is most suitable for disposal of the brines without monovalent cations and heavy metals as it can prevent the precipitation of such materials before disposal [40]. This method is usually used for municipal, industrial, and liquid hazardous wastes and requires a suitable geological circumstance [51]. It is necessary to evaluate the geological conditions of the injection site in detail and specify the depth and exact location of suitable porous media before drilling an injection well [52]. Deep well injection has the highest rate of capital cost among other disposal options. Finding an appropriate well site, corrosion and leakage of the wastes into the well casing, and subsequent groundwater contamination are the most important challenges regarding this disposal option [52]. Accordingly, this method is only used when there is no suitable alternative.

3.4 Application for land

In some situations, the brine can be used for vegetation such as parks, golf courses, and lawn irrigation, and land application of the brine can be suitable to reuse water for these purposes. This process can also provide the required nutrients for the plants. Different factors are affecting the selection of this option such as the existence and price of the land, expenses related to water dilution, cost of the irrigation equipment, infiltration rates, irrigation importance, salinity tolerance interval for desired vegetation, and groundwater quality regulations [53]. Based on the Food and Agriculture Organization (FAO) of the United Nations [54], the regulated concentration limits of Ca, Mg, and Na ions to irrigate the general crops are 400, 60, and 900 mg L$^{-1}$, respectively. Although brine may have negative impacts on the soil and groundwater when disposed in the land, the reuse of brine originating from livestock wastewater in the agricultural application as a liquid fertilizer is proposed by Yoon et al. [6]. This recommendation is only applied when there are no pathogenic microbes in the sample. The adverse impact on underground aquifers has been found by Mohamed et al. when the brine is directly disposed in some lands with permeable soil containing a low clay content and organic matter [38]. Increasing the concentration of the brine can reduce the permeability of the soil and consequently can reduce the crop yield. Therefore, based on the salinity tolerance interval of the crop for different ions, the brine must be diluted with freshwater to an acceptable range.

3.5 Evaporation ponds

In evaporation ponds, brine is directly under the sunlight and slowly evaporates in shallow, arrayed earthen basins. When the freshwater available in the brine has evaporated, the solutes in the brine are precipitated and then periodically removed from the site. The evaporation ponds are broadly used in some locations where
the temperature and dryness are high enough to evaporate water at the desired
time [55]. Since there are some critical concerns regarding groundwater pollution,
this method must be appropriately designed and performed. In general, based on
environmental regulations, the evaporation ponds are forced to be isolated from
underlying aquifers using the impermeable coating. In some situations with high
levels of rare metals, a pond with double liner has to be constructed. In addition,
when the ponds are not laminated or the point liner is damaged, some brine may
infiltrate the aquifer beneath the pond and reduce its water quality [56]. Some fac-
tors are affecting the selection of this disposal option such as the existence and price
of the land, climate circumstances, and underlying groundwater quality. The cost
range of this disposal method is from US$3.28 to US$10.04 based on 1 m$^3$ of brine
rejected and is the most expensive disposal option [43].

3.6 Conventional crystallizers

The brine contains some metals that can be recovered as an attractive solution to
avoid disposal problems with additional economic advantages. Thus, it is a critical
challenge for researchers and industrial activists to manage brine concentrate regard-
ing its beneficial resource recovery. During the recovery process, if rare and valuable
components are found, it can be considered as a double objective. This achievement
can enhance the overall economic efficiency of the treatment process by reducing the
adverse impacts of RO concentrate disposal on the environment. In the last stage of
the brine disposal process, some operations are performed for brine crystallization.
Compared to other disposal methods such as evaporation pond and deep well injec-
tion, the brine crystallizer process is expensive [40]. This process is only executable
where deep well injection treatment is expensive, evaporation ponds cost a lot for its
instruction, and the rate of evaporation is low. In Israel, a brine discharge from RO
plant is fed to a series of evaporation ponds after mixing with seawater and then pump
to a salt processing plant [57]. The evaporation and crystallization steps for salt recov-
ering from RO brine have been evaluated by Mohammadesmaeili et al. using lime soft-
ening in several stages of the evaporation crystallization processes [58, 59]. They found
that magnesium hydroxide, calcites, and CaSO$_4$ with the purity of 51–58, 95, and 92%,
respectively, were produced after lime soda treatment. Zero liquid discharge achieve-
ment by combining RO with evaporation and crystallization was noted by Seigworth
et al. [60]. Therefore, while additional study is required to evaluate the economic
aspects of salt production, using these methods for salt recovery is emphasized as a
sustainable option. Ahmed et al. used the patented SAL-PROC (Geo-Processors Inc.,
USA) processes to determine the sustainability of recovered salts from RO retentate of
a desalination plant by consecutive extraction of salts in the form of liquid, crystalline,
and slurry [61]. They specified that sodium chloride, CaCO$_3$, sodium sulfate (Na$_2$SO$_4$),
and calcium chloride were the most likely recoverable products that can provide the
potential cost-effectiveness of the desalination processes. It has been found by Ahmad
and Williams in another study that 45 million tons of salts are recovered yearly in the
USA and chemical industries use about 70% of this amount [62].

4. Common technologies for brine treatment

Brine contaminant is one of the main concerns due to hazard creation in the
environment. Therefore, it is necessary to remove them before safe disposal in
the beneficial use of reclaimed brine solution or open water bodies. Biological
processes, oxidation, and chemical precipitation coagulation can be used for the
treatment of brine.
4.1 Chemical precipitation process

Chemical softening has been broadly utilized for the brine treatment with lime softeners. High removal of scale-forming ions is the main advantage of utilizing the chemical softening framework for concentrate treatment. Be that as it may, the confinement of the method is the era of slime which needs additional care for legitimate management. Lime treatment method was utilized by Kolluri for removing the silica from the brine which results in the removal of silica content by 53–76% [63]. It was noted that lime treatment was exceptionally successful to remove silica from high silica brine and found that no silica removal happened until the lime dose surpassed the lime equivalent of the alkalinity [64]. Gabelich et al. have shown that the Ca substance was removed as CaCO$_3$ after elimination of silica and metals (such as Ba) by coprecipitation with Mg(OH)$_2$ [65]. In the absence of alkalinity, sodium bicarbonate was included in the brine to precipitate the Ca as CaCO$_3$. Be that as it may, the nearness of harmful overwhelming metal particles and developing natural contaminants in brine arrangement might prevent the immaculateness of the target compounds’ precipitation, and this still ought to be completely investigated.

4.2 Coagulation

Coagulation may be a basic physicochemical and commonly connected handle for organics’ evacuation from water and wastewater. The components included in coagulation are charge neutralization and adsorption of organics on the metal hydroxide [66, 67]. The type and dosage of coagulant used and the characteristics of the feedwater impact the efficiency of organics’ removal [68]. Coagulation has not been considered broadly for utilizing in brine treatment. This can be since brine contains an essentially high concentration of salts. Given the straightforwardness of the method, this method has been examined for eliminating the natural component from high saltiness brine arrangement. Umar et al. explored coagulation utilizing two aluminum-based [alum and aluminum chlorohydrate (ACH)] and two ferric-based coagulants [ferric chloride (FeCl$_3$) and ferric sulfate (Fe$_2$(SO$_4$)$_3$)] for treatment of high saltiness brine concentrate (EC of 23 mS cm$^{-1}$) and showed that at 1 mM dose, the DOC elimination for the two ferric-based coagulants was comparable (40–43%) while that for ACH was extraordinarily lower (14%) than for alum (23%) treatment [69]. Dialynas et al. examined the execution of alum and FeCl$_3$ coagulation for the concentrate gotten from a plant and showed that the DOC elimination was 42% for alum (beginning DOC, 8.5 mg L$^{-1}$) and 52% for FeCl$_3$ (starting DOC, 12.3 mg L$^{-1}$), with an ideal dose of 2 mM as Al$^{3+}$ and 0.4 mM as Fe$^{3+}$, individually [70]. This shows that iron-based coagulants are more effective than aluminum-based ones for brine treatment. Employing a higher concentration of FeCl$_3$ (1 mM Fe$^{3+}$) than Dialynas et al. [70], a lower evacuation of DOC of 26.4% (introductory concentration, 18 mg L$^{-1}$) from brine was detailed by Zhou et al. Comstock et al. examined the impact of Fe$_2$(SO$_4$)$_3$ doses (1.79, 4.48, 8.95 mM Fe$^{3+}$) for brine treatment (introductory DOC, 13 mg L$^{-1}$) gotten from a civil drinking water treatment plant [71, 72].

In spite of the fact that the initial DOC concentration of the brine arrangement was comparable with that of Dialynas et al., they utilized an essentially higher dose of coagulant (8.95 mM Fe$^{3+}$) for a comparative degree of DOC evacuation (58%) [70]. This was conceivably due to the diverse water source and in this way diverse organics’ characteristics. Compared to the already specified postulates, Bagastyo et al. found a lower expulsion of DOC of 52% for a starting DOC concentration of 42 mg L$^{-1}$ and 25% for a starting DOC concentration of 62 mg L$^{-1}$, with alum coagulation [73]. But, FeCl$_3$ gave a comparable elimination of DOC of 34% and 38%
for both tests. They have shown that the ideal measurement for both coagulants was 1.5 mM at pH 5. Researchers have shown that alum coagulation might eliminate up to 42% of DOC, while FeCl$_3$ might eliminate 52% at the same dosages [70]. Another research by Bagastyo et al. [59] has shown that FeCl$_3$ coagulation might eliminate 79% of color, 34% of DOC, and 49% of COD. The lower elimination of DOC and COD was due to the existence of a high percentage of low to medium molecular weight (MW) compounds within the brine solution. This was since this method was incapable to expel solvent natural compounds with a low MW because it might primarily expel high MW organics [74].

### 4.3 Electrocoagulation

Electrochemical treatment is an effective treatment innovation for the treatment of tall saltiness water because it guarantees a fabulous electric conductivity that might diminish the vitality utilization. This handle incorporates an electrolytic reactor with anodes (aluminum, press, or stainless steel) and a division tank in which feedwater is passed through a reactor, and coagulation/flocculation happens with the metal dissolved from the cathodes [75]. The metal anode dissolution is going with by hydrogen gas bubble arrangement at the cathode, coming about in capture of the flocs, and this at that point causes buoyancy of the suspended solids, inevitably eliminating the contaminants. The preferences of this method incorporate less slime generation than an ordinary coagulation method. The challenge of this method is the high operation and support costs related to anode substitution, high vitality utilization, and restricted full-scale plant involvement. Subramani et al. explored the impact of electrocoagulation for the treatment of brine, and it is known that this method was exceptionally productive in evacuating Ba, Ca, Mg, strontium (Sr), and silica with more than 90% expulsion [10]. Another research by Cave and Wang utilized electrocoagulation as a pretreatment step for the brine preparation for anticipating silica fouling and has shown that 80% of the silica was eliminated at a current concentration of 0.5 A and water-powered maintenance time of 30 min [76].

### 4.4 Oxidation-based technologies

#### 4.4.1 Ozonation

Ozonation has been broadly utilized for water and wastewater treatment, especially for the corruption and advancement of biodegradability of the natural compounds [77, 78]. The organics are oxidized either through a coordinate response with molecular ozone (O$_3$) which is profoundly particular or backhanded responses with free radicals (HO·) [79, 80]. This method was developed to treat brine either alone or in combination with other methods. Stand-alone O$_3$ was used by Lee et al. [81] and Zhang et al. [82] to degrade the organic content of brine solution with similar initial TOC and COD concentrations for both samples of 18 mg L$^{-1}$ and 60–65 mg L$^{-1}$, respectively. The impact of ozonation on the degradation of organic compounds from the brine solution was investigated by Zhou et al. [77]. It was shown that the elimination efficiencies of COD, DOC, and color were 14%, 22%, and 90%, respectively. Lee et al. [81] conducted a series of experiments to investigate the impact of reducing the organic compounds by using an ozonation method and showed that the TOC was reduced by 25% after 20 min of ozonation (at a 10 mg L$^{-1}$ concentration). They also found that the enhancement of TOC reduction was less than 2% after increasing the dosage from 6 to 10 mg L$^{-1}$, highlighting that it was difficult to remove the remaining organics using decomposition
via O$_3$. Lee et al. [81] have shown that the large MW organics were converted to low MW organics and explained the difference in the distribution of the organics’ fractions after brine treatment. Furthermore, they found that organics with an MW of 10–100 kDa were mostly reduced (36–72%) after 10 min, and the removal efficiency is improved by 20% when the contact time increased from 10 to 20 min. It was also shown that it is least likely to remove the organic compounds with a MW of >100 kDa. Most probably this was due to the surface trimming effect of O$_3$ which results in breakage of some of the bonds on the surface but incomplete molecule disintegration, resulting in bulk organic content intact [83]. By utilizing the O$_3$ process of brine treatment, Le et al. analyzed the process before using the biological activated carbon (BAC) process. They showed that only 5% of TOC will be removed if we use O$_3$ alone with 3.0 mg O$_3$ L$^{-1}$ with 10 min contact time. It was also observed that BAC treatment (60 min contact time) is capable of giving better removal of organics than O$_3$ alone (6.0 mg O$_3$ L$^{-1}$ with 20 min contact time), and combined O$_3$-BAC processes removed 88.7% of TOC and 69.8% of COD. This is mainly due to the usage of O$_3$ which results in an enhancement of the biodegradability of the organic compounds. This is ascribed to the effective breakdown of high MW aromatic compounds to low MW organics which is followed by appropriate biodegradation of the residual organics with the BAC system. As shown by Tambo and Kamei, the ratio of TOC/UVA254 is utilized to assess the performance of biodegradability, and they found that by 20 min of ozonation the ratio was enhanced from 35 to 107 [84]. This also approves the helpfulness of O$_3$ in breaking down the large MW organics and enhancing the biodegradability of the residual treated organics. It was shown that after 30 min ozonation treatment of the brine the COD removal was 19–25% [78]. The lower reduction was mainly due to the insufficient reaction of O$_3$ with the by-products. The combination of processes such as UV/A/titanium dioxide (TiO$_2$), ultraviolet A/hydrogen peroxide (UVA/H$_2$O$_2$), and O$_3$ was investigated, and they showed that the combined method was not effective at enhancing the DOC reduction compared to ozonation alone [46].

4.4.2 UV/H$_2$O$_2$ process

UV/H$_2$O$_2$ technology is of great interest to treat the brine solution [46]. Researchers found that treatment by UV/H$_2$O$_2$ can effectively remove the organic compounds over a wide range of MW, and the low MW organics react slower than large MW compounds due to the fact that smaller organics are less aromatic in nature and contained lower molar absorptivities, thus having a small number of reaction sites available to react with HO$.^-$ [85]. Application of UV/TiO$_2$ for the removal of the organic load from the brine concentrates was investigated in several research projects. Westerhoff et al. investigated the impact of an ultraviolet (UVC)/H$_2$O$_2$ method to treat the brine concentrate with an initial DOC concentration of 40 mg L$^{-1}$ and showed that 40% of DOC was eliminated by utilizing the 10 mM H$_2$O$_2$ at pH 4 [86]. A research conducted by Zhou et al. demonstrated poor performance of UVA/H$_2$O$_2$ to treat the brine where 10 mM H$_2$O$_2$ dosage at pH 4 could only reduce the 2.3 ± 2.8% of DOC [77]. The lower reduction was mainly due to the insufficient reaction of O$_3$ with the by-products. The combination of processes such as UVA/titanium dioxide (TiO$_2$), ultraviolet A/hydrogen peroxide (UVA/H$_2$O$_2$), and O$_3$ was investigated, and they showed that the combined method was not effective at enhancing the DOC reduction compared to ozonation alone [46].
An Overview on the Treatment and Management of the Desalination Brine Solution
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by Westerhoff et al. [86]. Furthermore, it was shown by Bagastyo et al. that the removal of dissolved organic nitrogen for both samples was insufficient (32 and 27%) [73]. This was mainly due to the high proportion of low MW organic compounds present in the brine sample which were positively or neutrally charged compounds with low reactivity to oxidation by the UVC/H$_2$O$_2$ process. The UVC/H$_2$O$_2$ method was investigated by Umar et al. in treating one moderate (EC $\sim$8 mS cm$^{-1}$) and two high-salinity (EC $\sim$23 mS cm$^{-1}$) municipal wastewater samples with different inorganic and organic characteristics [12]. It was shown that the difference in the reduction of DOC (26–38%) and COD (25–37%) over the tested saline conditions is very small. This indicates that the brine solution salinity did not have a substantial influence on the treatment of UVC/H$_2$O$_2$. It was also found that UVA254 and color reduction were substantially higher than for COD and DOC for all samples, indicating the larger humic compound breakdown. However, only few researchers have analyzed the impact of level of salinity on the performance of UVC/H$_2$O$_2$ for organics removal. TiO$_2$ suspension by UVA irradiation was investigated by Dialynas et al. [70] in treating the brine solution and showed DOC reduction after a 60-min reaction. This was mainly due to the enhancement of opacity caused by the suspension of catalyst. The impact of ozonation in treating the brine with/without UV/H$_2$O$_2$ was also explored and showed that O$_3$ only is capable for removing only 22% of the DOC; however, the combination of O$_3$ with TiO$_2$ and UV could improve the efficiency of removal by 52% [88].

4.5 Biological processes

One of the important factors affecting the efficiency of biological processes is the existence of high salinity in wastewaters. This is mainly due to the high-salinity concentration which results in unbalanced osmotic stress across the microbial cell, resulting in systems failure [89]. In addition, due to the existence of bio-refractory organic compounds in the brine solution, the biological processes are not very effective [77]. Häyrynen et al. demonstrated that the use of bioreactors to remove the nutrients and the existence of heavy metals such as chromium and Cu in the feedwater inhibit the efficiency of the nitrifying bacteria [90]. Ersever has conducted a research to investigate the several biological processes to remove the sulfate, nitrate, and NH$_3$ from the brine [5]. It was shown that at a temperature of 35°C, pH of 8.0, and C/N of 1:8:1, the maximum denitrification rates can be achieved. By considering the nitrogen as a minor pollutant in the waste stream, Ersever et al. investigated the impact of a fluidized bioactive absorber reactor method in removing nitrogen compounds from RO brines and showed that this technique is very effective to remove the nitrogen (90%) from RO concentrates [91]. As shown by Dialynas et al., the membrane bioreactor can effectively remove the organics from the RO concentrate [70]. It was shown that 90% of the organics from RO concentrate can be removed by activated carbon due to the adsorption of medium/small MW organics by the pores of the activated carbon [70, 77].

Ng et al. [92] and Lee et al. [13] investigated the removal of organic content using BAC columns. It was shown by Ng et al. that 39.6% of COD and 25% of TOC from brine solution with an empty bed contact time (EBCT) of 40 min can be removed [92]. So far most of the researches focused on using the BAC method for treating the brine with a TDS level of less than 2000 mg L$^{-1}$ [40]. A research by Vallero et al. demonstrated that biodegradation of methanol in a non-adapted granular inoculum sludge system can be completely inhibited by high NaCl concentration (25 g L$^{-1}$) [89]. Shi et al. demonstrated that a TDS concentration more than 14.92 g L$^{-1}$ considerably reduced the removal of COD by the upflow anaerobic sludge blanket and utilized an ion exchange resin pretreatment to eliminate the salt concentration present in the wastewater while holding the most portion of organics
in the wastewater and showed that 22% of the COD was eliminated together with the elimination of 80% of TDS [93]. Lu et al. investigated the impact of BAC with high salinity (TDS levels of 10 g L\(^{-1}\)) for treating the brine concentrate. It was shown that the reduction efficiency of COD and DOC was approximately 50 and 60%, respectively [94]. This indicates the effectiveness of biological treatment for activated sludge to be acclimated to high-salinity environments.

5. Membrane technologies

5.1 Forward osmosis

Contrary to the energetically intensive hydraulic pressure-driven reverse osmosis (RO), forward osmosis (FO) drives water through membranes due to osmotic pressure differences that are inherently present in the system. The driving force across the membrane is attributed to the differences in salt concentration and creates the osmotic pressure gradient [95]. Water moves from the feed (low salt concentration) to the draw solution (high salt concentration) [95]. There have been many multifarious studies conducted on FO applications, for instance, minimizing the leachate from sanitary landfills [95], reducing salt content in draw solutions [95–98], identification of fruit juice concentrations [95], provision of emergency water supply [99], reducing RO [100] and anaerobic digester concentrate [101], volume production, and lastly, treatment of wastewater with high salt content in petrochemical and fracking industries [101, 102]. A study conducted by Wang and Ng employed draw solution containing 5–6 M of fructose and treated reverse osmosis concentrates (ROC) consisting approximately 1.5 M of NaCl—passing through a FO membrane with a cellulose acetate matrix [100]. Feedwater recovery of approximately 75% was attained after 18 h; an initial flux of around 8.0 L/m\(^2\)/h\(^{-1}\) was also obtained [100]. McGinnis et al. used the draw solution consisting of NH\(_3\)/CO\(_2\) coupled with a thin-film composite (TFC) FO membrane for the treatment of highly saline water with a total dissolved solids (TDS) concentration of approximately 75,000 mg/L [102]. Water flux obtained averaged out to be 2.5 L/m\(^2\)/h\(^{-1}\) and a recovery of about 65% was attained. TDS concentrations from the FO process were in compliance with discharge standards of under 300 mg/L. Moreover, FO consumed about 40% less electrical energy than the forced circulation mechanical vapor compression (MVC) systems applied conventionally [102]. It was reported that by utilizing the draw solution consisting of 26% NaCl and a cellulose triacetate (CTA) membrane for produced water treatment, an average flux of 6 L/m\(^2\)/h\(^{-1}\) at recovery rate of 50% was recorded [101]. In Hancock’s study, FO process was utilized to treat produced water with TDS ranging from 70,000 to 225,000 mg/L. Data obtained showed that recovery averaged to be 60% with flux hovering around 3 L/m\(^2\)/h\(^{-1}\) [103]. The entire configuration in Hancock’s study was able to comply with the United States Environmental Protection Agency’s (USEPA) effluent standard—inclusive of heavy metals, radioactive matter, halides such as Cl\(^{-}\), and TDS. Boron concentrations of less than 0.05 mg/L were also met, a criterion to meet to achieve best practice in the agricultural sector [103].

The key in using FO in ROC treatment is the low energy consumption that comes with it. There is no need for external hydraulic pressure sources which are energetically intensive [95]. High TDS water exceeding 70,000 mg/L can be treated, making FO process suitable for ROC treatment. Figure 1 shows a FO schematic employed in ROC treatment. For mining sectors, a two-stage RO was recommended for recovery of the draw solution during ROC treatment [103], compared
to conventional thermal-based draw solution recovery systems. Overall feedwater recoveries amounted to nearly 90% with this configuration.

Other advantages of the FO process include a lower fouling propensity of the membranes than micro-, ultra-, and nanofiltration and reverse osmosis processes, which are all pressure driven. Unlike pressure-driven membranes, the effects of membrane fouling are also more reversible in FO membranes and can be minimized by optimizing the process and hydrodynamic parameters [104–106].

Despite the multifaceted benefits, the FO system is beset with flaws. FO membranes with high efficacy, coupled with the choice of draw solutions which should be easily separable and have high osmotic pressures, are common challenges in their manufacturing. Moreover, low water flux is common in the FO process, which is contrary to the flux expected given the bulk osmotic pressure difference and permeability of membranes used. The reason for such a discrepancy is the existence of internal concentration polarization (CP) [97]. Consequently, the FO processes need to be optimized to reduce the effects of CP and damage of membrane integrity due to membrane fouling. Despite the suitability for concentrate volume. Although the application of FO has been shown to be suitable for reducing the concentrate’s volume, improvements are still necessary to maximize recovery of draw solution. There are still no full-scale facilities using FO for minimizing the volume of concentrate till today [95].

5.2 Membrane crystallization

An extrapolation of membrane distillation (MD) application is membrane crystallization (MCr). MCr enables the simultaneous provision of potable water and precious crystalline salts [106]. On both sides of a hydrophobic and microporous membrane surface, it consists of a feed, which contains a solution that is nonvolatile and a distillate on the other [107]. The vapor pressure disparity between the two sides of the membrane creates a driving force that causes evaporation of volatile constituents, inclusive of water. This enables it to pass through the membrane and condense on the distillate side. The process continues until the induction of solution supersaturation and when the salt crystals nucleate. MCr systems display all the positive traits observed in the MD process, such as higher than average crystallization rates, well-controlled crystal nucleation, and growth kinetics [108]. However,
compared to MD, there are limited studies on MCr present in literature. In other study, both PVDF and PP hollow fiber membranes were employed for lab-scale and semi-pilot scale MCr processes, achieving a water recovery of approximately 40% and almost 16.5 kg of NaCl salt crystals (99.9% purity) from 1 m$^3$ of high-saline feed solution that has a TDS concentration of nearly 250,000 mg/L [109]. Quist-Jensen et al. propound that both MD and MCr can be applied in industrial wastewater treatment containing high Na$_2$SO$_4$ content as well as direct treatment of wastewater that has not been subjected to any forms of filtration, i.e., nanofiltration [110]. The SEC and treatment costs in MCr are slightly higher than in MD, weighing in at approximately 40–75 kWh/m$^3$ and US$1.25/m$^3$ of freshwater produced, respectively [109, 111].

5.3 Membrane distillation

Membrane distillation (MD) relies on the fundamentals of evaporation and the separation of two or more aqueous solutions at different temperatures. A gas-liquid interface is created as volatile constituents are transferred through a microporous hydrophobic membrane [112–114]. MD occurs when there is a difference in the solution’s partial pressure on both sides of the membrane [115]. If the solution’s vapor pressure is higher than the condensate’s vapor pressure, evaporation will occur. There are many permutations in the types of MD configurations, but for desalination purposes, direct contact membrane distillation (DCMD) is the preferred choice. In this process, an aqueous cooler distillate stream flows on one side of the hydrophobic membrane, while hot brine flows on the other. Water vapor passes through while repelling the liquid molecules due to the hydrophobic properties of the membrane [95].

When water vapor evaporates from the hot brine at the periphery of the brine-membrane interface, it diffuses through hydrophobic membrane pores which are filled with gas. The water vapor then condenses in the membrane interface at the side whereby the cooler distillate flows. By heating the feedwater, vapor pressure is increased and thus enhancing the driving gradient for vapor production [116]. Using MD alongside a crystallizer for the treatment of ROC with a conductivity of 15 mS/cm, Tun and Groth obtained an average flux of 4 L/m$^2$h$^{-1}$ and an overall feedwater recovery of 95% [117]. The use of a vacuum multi-effect membrane distillation (V-MEMD) system was employed to treat concentrates of thermally desalinated seawater and improve the recovery of feedwater. Figure 2 shows a schematic of this process. TDS in the thermally desalinated seawater's concentrate was 100,000 mg/L, and the flux of the four-stage V-MEMD system was approximately 5 L/m$^2$h$^{-1}$ [118]. Although the flux from a V-MEMD system was five times lower than that of a DCMD system, the former was less energetically intensive due to the utilization of waste heat to raise the feed’s temperature. In addition, having the membrane to be staged in series resulted in downstream condensation of vapor, and overall energy input is reduced because it is transferred back to the feed [118]. MD supersedes other desalination processes because operating temperatures need not exceed 70°, which is lower than the minimum temperature requirements of a conventional distillation process [119]. MD can also be retrofitted with heat sources such as renewable solar energy, geothermal energy, or waste heat sources [119]. In addition, MD efficacy is hardly affected by the CP phenomena, which enables high salt concentrations nearing saturation limits to be fed into the process. However, since MD is always associated with a low permeate flux compared to RO membrane processes [119], studies of several polymers—polypropylene (PP), polytetrafluoroethylene (PTFE), polyacrylonitrile (PAN), and polyvinylidene fluoride (PVDF)—have been conducted to circumvent this issue [120, 121]. The pivotal reason why
a single-layer PVDF membrane had lower decreases in membrane permeability was primarily attributed to its morphology and pore size as compared to the wall thickness of the membrane [121]. This was also in comparison to dual-layer hydrophobic-hydrophobic PVDF and dual-layer hydrophobic-hydrophilic PVDF/PAN membranes. In an alternative research, the MD polymer matrix was modified to maximize permeability by inserting carbon nanotubes. Incorporation of such nanotubes provided higher contact angles (113°), higher porosity (90%), and lower thermal conductivity [122].

6. Brine adaptation for industrial use

6.1 Brine adaptation for chlor-alkali industry

At saturated concentrations at around 300 g/L, brines containing NaCl are required to be fed into electrolytic cells for generating chlorine and sodium hydroxide. The NaCl brine must be rid of organic detritus and alkaline earth metals like strontium (Sr), barium (Br), magnesium (Mg), and calcium (Ca). Notably, Melián-Martel et al. propounded to employ a multi-effect evaporator coupled with chemical precipitation to remove Ca, \( \text{SO}_4^{2-} \), and Mg in the treatment of seawater RO brine for the chlor-alkali process [123]. To validate the efficacy of the system, concentrated brine of approximately 8500 m\(^3\)/day from the Pozo Izquierdo desalination plant, Gran Canaria was used as the feed source to be treated. The production capacity of the said desalination plant is about 35,000 m\(^3\)/day with a conversation efficiency of 50%. An electrolyzer was used to assess the chlorine and sodium hydroxide production of the treated brine. The proposed system attained the production of 102 kilo tons/year of chlorine, 254 kilo tons/year of sodium hydroxide, and 3 kilo tons/year of hydrogen gas after treating the seawater RO brine. Table 2 depicts the compositions of the products. A common practice to offset the cost in the chlor-alkali industry is to sell the concentrated brine to another industry. From a cost-base perspective, it is economical to produce brine from reverse osmosis concentrate than to create brine from raw seawater. Melián-Martel et al. gave a rough estimate of 2000 kWh required per ton of NaOH generated. Moreover, the 3

[Figure 2. Process schematic of MD process for RO concentrate treatment (adapted from [118]).]
kilotons/year of hydrogen gas generated could be used to generate electricity and minimize the amount of energy required. This makes the process suitable in places where energy resources are expensive or scarce. On a similar vein, brine adaptation for the chlor-alkali industry is not land intensive, which contributes to the reduction of capital costs, alleviating the strain on resources in land expensive or scarce countries [123].

Despite the positive attributes derived in brine adaptation for the chlor-alkali industry, there are problems associated with it as well. RO brine contains higher divalent cation concentration, which necessitates removal procedures involving high costs. To circumvent this problem, production of NaCl needs to occur first before generating the necessary brine of a specific matrix.

In the salt manufacturing industry, Tanaka et al. propounded that energy consumption via electrodialysis of seawater RO brine was 20% less than raw seawater [124].

6.2 HCl and NaOH production with bipolar membrane electrodialysis

The mechanism of membrane electrodialysis involves two aspects—applying a potential across the membrane to enhance mobility of ions and to limit their movement via selective membranes. To split water into its hydrogen ions (H\(^+\)) and hydroxide ions (OH\(^-\)), the application of electrodialysis is done in conjunction with a bipolar membrane—hence the name bipolar membrane electrodialysis (BMED) [125]. The combination of hydroxide ions and cations and combination of protons and anions lead to production of acid and base respectively. Figure 3 shows the diffusion of ions across the membrane in a BMED system. Badruzzaman et al. propound the employment of BMED as the final step for generating hydrochloric acid and sodium hydroxide from high-salinity solutions after undergoing sequential treatment steps of using membrane bioreactors, coupled with reverse osmosis and softening via calcium hydroxide. The entire system is known as an integrated membrane system (IMS) [126]. In Badruzzaman et al.'s study, the salinity of the feed was about 3 g/L, which deviates greatly from seawater or brine water salinity. Research also validates that electrodialysis accumulates major positive cations and negative anions in the acid and base chamber, respectively. Water after the treatment process can be used directly as product water or subject to further reverse osmosis treatment for further purification. The authors compared the capital costs for IMS implementation. The different permutations are as follows: the first involved a sequential MBR and RO followed by an evaporation pond for disposal. The second permutation revolved around a zero liquid discharge thermal process via a concentrator and a crystallizer. The capital and yearly operational and maintenance (O&M) costs for first option are approximately $1.65 and $0.41/m\(^3\), while that of the second option are $0.50 and $0.80/m\(^3\), respectively. IMS, on the other hand, only requires $0.43 and $0.25/m\(^3\). These cost values for the IMS do not factor in the profit margin of selling the acid and base produced, which are chemicals of high demand, alongside the cost of recovered water. The O&M costs can be alleviated by

<table>
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<tr>
<th>Cl(_2)</th>
<th>NaOH</th>
<th>H(_2)</th>
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<tr>
<td>Cl(_2) &gt; 98%</td>
<td>NaOH—32%</td>
<td>&gt;99.9%</td>
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<tr>
<td>H(_2) &lt; 2%</td>
<td>NaCl &lt;20 ppm</td>
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Table 2. Composition of end products of chlor-alkali electrolytic process [123].
up to $0.1/m^3$. Unfortunately at present, BMED is not applied at an industrial level because the electrolytic cells applied are not as commercially established.

7. Metal recovery

Sixty elements from the periodic table are usually existed in seawater that some of them are rare and more valuable. Precious metals are valuable components in seawater, and their recovery from the rejected brine has long been considered for their advantages due to the relatively high levels in retentate brine. Based on several physicochemical, economic, and technical aspects, Dirach et al. suggested a protocol to recover elements of interest from concentrate. This process uses evaporation to increase the concentration of solution up to about 200 g/L before the first recovery step to extract phosphorus precipitation using an alum blend of iron sulfate and aluminum sulfate [127]. Then a liquid-liquid extraction is applied by adding HCl to recover cesium from the solution. Another liquid-liquid extraction will be performed using an organic phase, consists of three different acids for indium recovery. A countercurrent process with 15 stages is essential to have an effective separation. Indium with a purity of 97.4% and also gallium with a purity of 99.8% will be recovered as a result of this process. Rubidium is then extracted by means of cation exchange resins. Potassium and rubidium are the first and second most attracted elements, respectively. To separate these two elements from the solution, it is necessary to increase the purification. In the next step, germanium will be undertaken which is crystalized to form germanium dioxide (GeO$_2$). The crystalized form of germanium is then exposed to gaseous HCl to be oxidized and then will be reduced to pure germanium by roasting in a reducing atmosphere of H$_2$. The main components contributing the remaining solution are mainly magnesium,
potassium, and NaCl. The solubility differences between these compounds are used to separate them from each other. The potential of recovering valuable metals (uranium, rubidium, cesium, lithium) from RO brine related to a plant in El Prat de Llobregat, Spain, using a number of sorbents, has been studied by Petersková et al. [128]. It was concluded that the best sorbent for both cesium and rubidium between all tested ones was hexacyanoferrate-based extractant Cs-Treat, while all tested sorbents were effective enough at sorbing lithium. The resin containing phosphonic and sulfonic groups has the highest tendency for uranium(VI) sorption. Even more importantly, though, the results showed that the salinity is a crucial factor affecting cesium sorption affinity onto Cs-Treat. Single-metal systems are moderately different from bimetallic systems based on the sorption results, which is due to the independency of sorption capacity from co-ion effect, and accordingly Cs-Treat was highly selective for cesium and rubidium [125]. By utilizing metal recovery, novel and abundant sources of many valuable and rare metals can be provided from all over the world which can greatly increase its potential profitability [125].

As an example, in many countries where the conventional process is not available to produce non-carbon energies, uranium recovery would provide a non-carbon source of energy. In terms of environmental prospective, the impacts of metal recovery are much lower than mining, although the new technologies involved in metal recovery are still far from ideal conditions and require more improvement to be competitive with traditional process. Accordingly, this technology needs more attention and research to increase productivity and improve performance in metal recovery process and also adequately develop to be exploited on an industrial scale [125].
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