Brine Effluents: Characteristics, Environmental Impacts, and Their Handling

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Abstract. Brine discharge is one of the largest sources of wastewater from industrial processes. Because of the environmental impacts arising from improper treatment of brine discharge and more rigorous regulations of pollution control, industries have started to focus on waste minimization and improving the process of wastewater treatment. Several approaches have been proposed to provide a strategy for brine handling by recovering both brine and water or to remove pollutant components so it complies with environmental regulations when discharged. One of the most promising alternatives to brine disposal is reusing the brine, which results in reduction of pollution, minimizing waste volume and salt recovery. The brine may also contain valuable components that could be recovered for profitable use. Also, water recovery from brine effluent is generally performed to save water. In the case of rejected brine from desalination plants, water recovery from higher brine concentrations has huge potential for salt production. This paper gives an overview of different types of brine effluents, their sources and characteristics. Also discussed are impacts of brine on the environment and management options related to their characteristics.

Keywords: *ballast water; brine disposal; desalination; spent regenerant; wastewater.*

1 Introduction

Recently, due to the rapid growth in industrial activities, the world is facing a challenge in maintaining water supply, including protection of its quality and resources. Since the supply of quality water is decreasing, there is a growing need for wastewater reuse and recycling from industrial effluent. Meanwhile, to meet the stringent regulations of pollution control, industrial wastewater treatment techniques are evolving rapidly in view of various environmental issues. One of the largest sources of wastewater from industrial processes is brine discharge. Brine effluents are generated from various processes, such as: (1) desalination, (2) spent brine from ion-exchange regeneration, (3) ballast water, etc. Brine effluents have a strong negative impact on the environment due to their high concentration of salts and other pollutant contents [1-5]. The types of pollutants vary depending on the source. As for the aforementioned examples, desalination concentrates contain a higher salt concentration than

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seawater (used as feed for desalination plants) and they are also contaminated with several chemicals utilized during the desalination process. Spent brine regenerant is a brine effluent that comes from ion-exchange processes and is polluted with resins, multivalent ions of softening plants or organic contaminants [6-8]. Meanwhile, ballast water is seawater containing wide varieties of microorganisms, which may conflict with the different ecological environments wherein it is discharged [9].

Although brine effluents have a negative impact on the environment, they are commonly discharged without any further treatment. Because of more rigorous environmental regulations, industries have started to focus on waste minimization and options to reuse their wastewater, especially brine wastewater. In order to be reused, waste brine should be treated with suitable techniques to obtain the desired water quality. Moreover, brine effluents are also considered as a potential source for valuable uses that may bring cost minimization. In the case of rejected brine from desalination processes, the brine can be treated in a dual-purpose plant that performs simultaneous water recovery and salt production. The sale of the salt product could reduce the net cost of the overall process. Several integrated desalination processes (dominated by the application of advanced membrane-based processes) have been proposed to achieve this promising and interesting dual-purpose scheme of simultaneous desalination and salt production processes [10,11]. This paper is organized to cover several brine effluents and approaches of brine management according to their characteristics.

2 Sources and Characteristics of Brine Effluent

Brine effluents contain a high concentration of salt generated through various processes. Evaporation and concentration of seawater are typical examples of processes that produce brine as effluent. Brine solutions are also utilized in industrial processes for various purposes. However, due to contamination during the process, the brine solutions are generally disposed directly as effluent, without any further treatment. Some types of brines along with their typical characteristics are summarized in Table 1.

Rejected brine from desalination plants contains a high concentration of salt (usually higher than that of its original feed water) and also chemicals imparted during the desalination operations. Another type of brine is the spent brine regenerants that are produced by ion-exchange plants during the regeneration process. Its characteristics depend on the components adsorbed by the resins and also the initial salt concentration.

Table 1 Typical characteristics of Brine Effluent.

Types	Characteristics (components) and sources	References
• Rejected brine from desalination plant	• High salt concentration (TDS > 40 g/L) and hardness, containing heavy metals and chemical compounds used in process (anti-scalant, cleaning agent, etc.), higher temperature than ambient (employed in thermal-based processes such as MSF)	[5, 12]
• Spent brine regenerant	• High salinity (about 50 g/L or higher), hardness, and organic compound content (example: decolorization plants)	[13, 14]
• Blow-down water	• High salinity, TSS, and TOC content (example: SAGD evaporator and boiler with TDS of 50-300 g/L)	[15, 16]
• Rejected bittern brine from salt ponds	• High salinity (up to 400 g/L, mostly contains Na, Mg, K, Br, etc.)	[17]
• Ballast water	• Seawater containing aquatic species including micro-organisms, seaweeds, micro-algae, small invertebrates, eggs, spores, seeds, cysts and larvae of various aquatic plants and animal species	[18]

Notes: SAGD – steam assisted gravity drainage; TDS – total dissolved solids; TSS – total suspended solids; MSF – multi-stage flash distillation; TOC – total organic carbons

Meanwhile, in the production of heavy oils and bitumen resources, steam-assisted gravity drainage (SAGD) is generally utilized to reduce bitumen viscosity and increase oil production [19,20]. During the oil production process, water is generated while the earth is being drilled. The produced water is recycled and treated for use as boiler-feed water. Due to solute build-up during the recycling process, boiler blow down is required. Usually, the blown down water from SAGD is trucked and disposed into deep wells resulting in high operating costs, which could be the second largest production cost next to the oil production cost [15].

Solar ponds or solar salterns are traditionally employed to produce salt from seawater. During the evaporation process, various salts are precipitated in different stages, whereby the brine remaining in the ponds mainly contains magnesium chloride ($MgCl_2$) after NaCl precipitation [21]. The remaining brine (known as bittern salt) is usually considered a byproduct. The disposal of the bittern brine is not considered a serious environmental issue since it can be treated to recover valuable components [22]. It can be further processed to recover magnesium, potassium, bromide, boron, and other constituents as valuable products [23].

Although ballast water does not contain a high concentration of salt compared to several counterparts in Table 1, it is also considered a brine effluent. Ballast water is carried by ships to ensure stability, trim and structural integrity during the journey of the ships [24]. Usually ballast water is pumped into the ballast tanks when a ship has delivered cargo to a port and departs with less or no cargo. The ballast water is discharged again when the ship loads cargo. It is taken from one location and can be discharged into other environments that are highly likely to have different ecosystems. Since the microorganisms, algae, seaweeds, etc. in the ballast water are different from those in the original environment, this may pose an ecological threat to the location where the ballast water is discharged. Therefore, the ballast water should be treated first to eliminate any microorganisms it carries.

Brine effluents are also generated by processing of foods, such as canned meat, pickled vegetables, dairy products or fish and by leather industries [25]. In the food industry, brine effluent is generated during canning and pickling. Pickling, chromium tanning or soak liquor generated in the leather industry may contain about 80 g/L of NaCl [25]. The brine effluents generated in these industries are heavily polluted with organic substances. Therefore, the treatment of these brine effluents must be focused on organic compound removal.

3 Brine Discharge Impact

Roberts, *et al.* [26] classified the impact of brine disposal into physiochemical and ecological impacts. The physicochemical impact is attributed to their salinity, temperature and constituents that could alter the physicochemical properties of the receiving water. This alteration may have adverse effects on marine life. For example, elevated salinity of the receiving water body could be harmful for organisms due to the change of the water's osmotic pressure. Consequently, it could change the equilibrium osmotic condition between the water and the organisms, which can damage the cells of the organisms. The brine may also contain toxic components such as heavy metals that may harm aquatic organisms.

Hoepner, *et al.* [27] have reported a case study of the chemical impact of a seawater desalination plant at the northern Red Sea. The effects of chlorine (employed in RO membranes as anti-biofouling agent) and copper in the brine are considered a serious environmental issue, associated with the high toxicity of chlorine and the accumulation of copper in the sediment. Meanwhile, the content of anti-scaling agents in the brine is also of great concern due to their low degradability. Furthermore, a study has pointed out that beach erosion should be taken into consideration for assessing the environmental impact of brine discharge into the sea from coastal desalination plants [1] as brine outfall contributes to beach erosion. Mohamed, *et al*. [28] investigated the impact of brine disposal from inland desalination to the soil and groundwater. They reported that improper disposal of reject brine (particularly its disposal into unlined ponds or pits) could result in creating pollution of the ground water and soil. The increase of salinity due to intrusion may reduce plant and soil productivity.

In the case of spent brine regenerant from the ion-exchange softening process, the brine contains multivalent ions. The discharge of the spent brine regenerant into a disposal well requires attention to the scaling tendencies in plumbing systems. Anti-scaling agent should be incorporated during the injection of the brine, which increases the cost of discharge. Meanwhile, spent brine containing organic matter can hardly be treated in conventional sewage systems [29]. The high concentration of salts also causes problems for biological activities, so salt-tolerant microorganisms are required to digest the organic substances in the spent brine.

Aquatic bio-invasions that cause impacts to receiving ecosystems during ballast water discharge have been reviewed in the literature [18]. For example, some cholera epidemics (due to the *Vibrio cholera* bacteria) are seen as the result of ballast water discharge. Another example of the adverse effect of improper discharge of ballast water is algae blooming. This may cause massive killing of marine life through oxygen depletion or release of toxic components (depending on the species and the toxicity of the algae).

Due to its environmental impact, regulations have been introduced to set standards for brine discharge. The regulations and salinity limits for desalination brine discharge in some countries have been reviewed by Jenkins *et al*. [30]. According to this report, each country has a different standard, with the lowest incremental salinity limit ≤ 1 ppt. Meanwhile, regulations for ballast water have been provided by the International Maritime Organization (IMO). The regulations outline the ballast water performance standard, which states the limits of specific organisms, such as < 1 cfu/100 mL of toxigenic *Vibrio cholera* and < 250 cfu/100 mL of Escherichia coli, etc. [31]. These regulations are provided to avoid environmental impact of brine discharge.

4 Brine Management

4.1 Brine Discharge Options

Brine discharge options are tabulated in Table 2, classified into the following methods: (1) direct discharge; (2) energy-intensive discharge; (3) evaporation-treated discharge; and (4) land applications. From these options, it can be clearly observed that direct discharge, especially surface water discharge, incurs relatively low capital, operation and maintenance costs. On the other hand, some additional treatments may need to be applied in order to mitigate the potential impact of surface discharge, such as blending, mixing zone, use of non-toxic chemicals, pH adjustment, and diffusers [32]. If an existing wastewater treatment system is close to the plant, sewer disposal would be an interesting alternative, since its discharge requires low cost and energy. However, the components of brine can reduce the ability of biological processes to treat the organic compounds when a large volume of brine is discharged into the wastewater treatment system [33]. For large amounts of disposed brine (larger than sewer discharge), deep-well injection is suitable, especially for inland desalination systems. However, deep-well injection comes with high capital costs, it is likely to contaminate the groundwater, and it may trigger earthquakes [22].

Table 2 Brine discharge options [33-39].

Classification	Options
Direct discharge	Surface discharge into: lake, reservoir, ocean, river
	Sewer discharge
	Deep-well injection
Energy-intensive discharge	Brine concentrator
	Crystallizer
	Spray dryer
Evaporation-treated discharge	Evaporation pond
	Solar evaporation
	Wind-aided intensification of evaporation (WAIV) technology
Land application	Irrigation of salt tolerant crops and grasses
	Fish farming
	Spirulina cultivation

Due to the disadvantages of direct discharge of brine, the methods of treating brine by applying thermal or related energies are emerging. Evaporation ponds are relatively easy to construct, require little labor to operate, require no mechanical equipment except for pumps, thus bearing low maintenance and operation costs [37]. However, they require a large area of land and thus result in very high capital costs. Moreover, since solar energy is used, the technique relies on appropriate ambient temperatures and is climate-dependent. Leakage due to inappropriate liners of the ponds also potentially has an impact on the environment.

To overcome the problems of solar evaporation ponds, WAIV (wind-aided intensification of evaporation) technology was developed as an alternative. The WAIV method exploits wind energy to evaporate wetted surfaces that are packed at a high density per footprint [38,40]. This method is based on vertically mounted and continuously wetted evaporation surfaces at 20 m^2/m^2 or higher packing densities. By using WAIV technology, the evaporation capacity is increased to more than 10 times over natural evaporation ponds, thus reducing the footprint of the land area required [38].

To push the limits of minimizing the amount of discharge brine, the zero liquid discharge (ZLD) method has emerged. It employs brine concentrator, crystallizer or spray dryer to recover solid contents from brine [34]. However, since the ZLD system for brine application is complex, consumes a huge amount of energy, and incurs high capital costs, it is not widely applied in industries [34].

Besides the direct and energy-intensive brine discharge methods, land application, or irrigation discharge, has also been developed, although its application is quite limited. It depends solely on land availability, local climate, vegetation tolerance to salinity and the location of the groundwater table [32]. Furthermore, the number of plant types that can grow in high salinity water conditions is very limited, not to mention the salinization of soil that may pose a serious constraint for large-scale application of this method.

4.2 Brine Treatment Methods

4.2.1 Treatment of Brine Effluent from Desalination Process

To reduce the negative environmental impacts of direct brine discharge, brine effluents are repurposed by some advanced treatments (most of which are membrane-based techniques) with several objectives, as summarized in Table 3. The new purposes for the rejected brine from desalination plants are water recovery, salt recovery or salt production, recovery of valuable metals, and other beneficial uses of the brine. In so doing, water recovery is conducted simultaneously with salt production in a dual-purpose plant [41]. As more water is recovered in the recovery process, more concentrated brine is generated, which is suitable for salt manufacture.

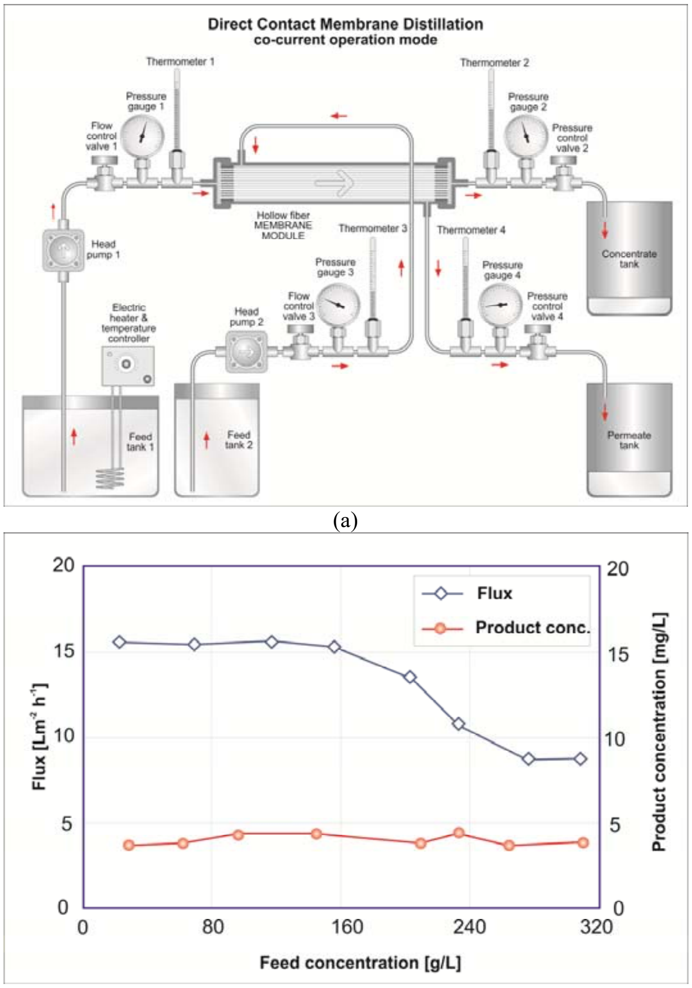
For example, Tanaka, *et al.* [42] reported the application of electrodialysis (ED) in salt production by using brine discharge from a SWRO (seawater reverse osmosis) plant. An ED unit was utilized as a pre-concentrator installed before the evaporator. The results of this study showed that energy consumption in the salt manufacturing process using brine discharged from a SWRO plant was 80% from that of the energy consumed in the process using seawater (in other words, it imparts a 20% cost reduction). ED reversal (EDR) has been proposed to control fouling due to precipitation of calcium and magnesium on the ion-exchange membrane [43]. In EDR, the polarity is reversed periodically to pull back the foulant from the membrane. By using this scenario, EDR can improve the degree of salt saturation up to 360% and improve total water recovery in combination with RO. However, ED is still subject to further improvement to reduce energy consumption in order to meet industrial requirements.

Membrane distillation (MD) is another potential alternative for water recovery and salt production. MD can recover water from brine with high purity and produce a solution containing a high solute concentration simultaneously (Figure 1). However, the major challenge of MD applications is the fouling due to the precipitation of organic or inorganic components that instantaneously reduce membrane permeability. There are cases where fouling occurs in MD during the treatment of brine from an RO plant due to the precipitation of calcium on the membrane. This can be easily washed away by using water [44], but it is also possible that the fouling causes permanent damage to the membrane [45]. Another challenge of the MD process is the wetting phenomenon. This phenomenon can increase mass transfer resistance. Recently, many modifications of membrane surface characteristics have been reported [46,47]. The use of a membrane with high hydrophobicity is expected to suppress the wetting phenomenon in the MD process.

Besides salt, seawater also contains valuable metals that can be recovered for profitable use. However, the development of the processes to extract these metals is still in progress due to difficulties in targeting the selected components. In addition, the process is very complex and requires multiple sequential steps [48,49].

Iodine and its derivative compounds have a high economic value due to their various applications in many different industries. Brine from desalination plants may also contain iodine, which may be recovered as a valuable byproduct [50]. Brine water consists of iodine in the form of an iodide salt. Therefore, oxidation of the iodide ions is required to obtain iodine. The oxidation of iodide to iodine using ozone as oxidation agent in the membrane contactor used as contacting device has shown promising results for iodine recovery from brine [51]. Compared to conventional contacting devices, the membrane contactor has some advantages, such as better contacting performance, larger interfacial area, and ease of direct scale-up [52,53]. With these advantages, this method could potentially be interesting for recovering iodine from brine.

Another membrane technology application with future potential is in the field of power generation from the salinity gradient between seawater or brine disposal and fresh water by using pressure-retarded osmosis (PRO) and reverse electrodialysis (RED) [54]. PRO uses a semi-permeable membrane that allows the transport of water from a low-concentration solution (such as a river, brackish or treated waste water) into a high-concentration draw solution (sea water) [55]. Energy is generated by using a hydro-turbine in which the kinetic energy of the flowing water is converted to electricity.



(a)

(b)

Figure 1 Direct contact MD (DCMD) for recovery of waste brine from MSF: (a) schematic of DCMD and (b) flux and product of DCMD in various feed concentrations (feed velocity = 0.5 m/s; permeate velocity = 0.07 m/s; feed temperature = 90°C; permeate temperature = 35°C) [56,57].

In RED, a number of anion and cation exchange membranes are stacked together in an alternating pattern between anode and cathode to allow the selective transport of salt ions [58]. Due to the salinity gradient of the two different solutions fed into the RED cells, chemical potential is converted to electrical potential by transporting ions from the high salinity solution to the low salinity solution. Integrated SWRO-PRO and SWRO-RED are promising processes to alleviate water and energy demands. Post, *et al.* [59] compared the power density and energy recovery performances of PRO and RED by mixing different types of saline water, i.e. seawater and brine, with river water. They showed that higher potential maximum power density could be achieved with RED (2-4 W/m^2) than with PRO (1.2-1.5 W/m^2) when these membranes are applied in seawater and river water. When applied to brine water, the PRO membrane seems to be more attractive with its higher power density and energy recovery (up to 15 W/m^2) [60]. By using these methods, not only electricity can be generated but also the salt concentration of the brine can be reduced.

To achieve the purpose of ZLD and the dual purpose of simultaneous desalination and salt production, several integrated desalination processes have been proposed. These processes yield zero or near zero liquid discharge, increased water recovery, and profitable salt production that can be used to offset the overall fresh water production cost. They include a combined membrane-thermal desalination process and an integrated membrane processes. As shown in Figure 2, which analyzes the costs of both production of fresh water and salt (in \$/m^3) by using integrated processes, it can be seen that Scheme 2 consisting of MF/NF/RO/MCr (microfiltration, nanofiltration, reverse osmosis, and membrane crystallization) is the most feasible scheme due to the profit generated by the salt sale, which is higher than the cost of fresh-water production.

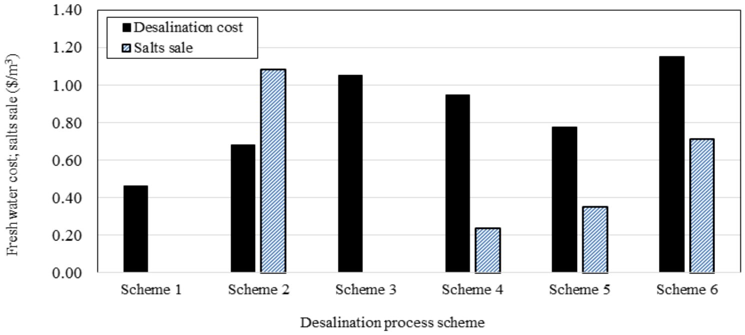


Figure 2 Cost of fresh-water production and salts sale per water produced by different integrated processes. Scheme 1: MF/NF/RO; Scheme 2: MF/NF/RO/MCr; Scheme 3: ED/EDR; Scheme 4: UF/NF/MSF/crystallization; Scheme 5: UF/NF/RO/MSF/crystallization; Scheme 6: ED/MSF/crystallization. Data collected from [11,43,61,62].

4.2.2 Treatment of Spent Brine Regenerant

The most promising alternative for handling spent brine regenerant is brine reuse. The technologies that can be used for this purpose are chemical precipitation, nanofiltration membranes (NF), biological treatment, and membrane bioreactor processing (Table 3). The chemical precipitation process (using sodium hydroxide) consists of several steps, including precipitation, neutralization using acid, and salt make-up [63]. As reported in the literature [63,64], chemical precipitation has the following advantages: reduction of regeneration and waste brine costs by almost 90% in comparison to waste hauling (thus rendering waste hauling unnecessary) and delivering significantly reduced cost of water for regeneration. Meanwhile, the chemical cost is slightly increased compared to that of sewer disposal due to alkaline solution consumption for precipitation. Overall, chemical precipitation gives a satisfactory cost for brine disposal treatment in ion-exchange softening plants. It should be noted that supplementary clarifier is needed for the precipitation process. A large volume of clarifier may be needed if this process is going to be used for treatment of large volumes of brine.

Nanofiltration (NF) is a membrane-based process with high rejection towards bivalent and multivalent ions while providing low to moderate rejection for monovalent ions, which is useful for regeneration of spent brine from softening plants. Due to its capability of removing organic substances, NF may also be used for brine regeneration in decolorization plants or other brine contaminated with organic components [65]. However, due to the high concentration of the brine, additional acidification or an anti-scaling injection is required. Furthermore, NF requires high pressure to drive the high flux and rejection.

Table 3 Brine effluent treatment: purposes and technologies.

Purpose	Technologies	References
Rejected brine from desalination plant		
• Water recovery	• CDI, ED, EDR, FO, MD, VESEP	[44, 66-70]
• Water and salt recovery (salt production)	• ED, MD, MCr, SAL-PROC process	[42, 71-73]
• Beneficial reuse (HCl and NaOH production)	• Bipolar membrane ED (BMED)	[74]
• Recovery of valuable metals (P, Ce, Cs, In, Ge, etc.)	• Extraction and adsorption	[48,49]
• Energy generation and brine dilution	• RED, PRO	[75, 76]
Spent brine regenerant		
• Partial reuse and discharge	• Partial recycling	[63]
• Water reuse	• RO, MD	[13, 77]

Table 3 ***Continued.*** Brine effluent treatment: purposes and technologies.

Purpose	Technologies	References
• Brine reuse	• Chemical precipitation, NF, biological treatment, MBR	[14,64,78-80]
Ballast water		
• Physical treatment	• Crum rubber filtration, micro-pore ceramic filtration, hydrocyclone, UV, heat treatment, ultrasound, GloEn-Patrol ^{TM} system	[81-87]
• Chemical treatment	• Ozone, ClO_2, NaOCl, Seakleen®, ParaClean® ocean	[88-92]
• Electro-chemical treatment	• Electrolysis	[24]
• Advanced oxidation process	• UV/Ag-TiO_2+O_3	[93]
• Combined treatment	• Micro-pore ceramic + filtration + UV; hydrocyclone + chemical disinfectant	[82,94]

Note: CDI – capacitive de-ionization; ED – electrodialysis; EDR – electrodialysis reversal; RED – reversed electrodialysis; FO – forward osmosis; MD – membrane distillation; MCr – membrane crystallization; NF – nanofiltration; PRO – pressure retarded osmosis; RO – reverse osmosis; UV – ultraviolet; VESEP – vibratory shear enhanced process.

Membrane bioreactor (MBR) processing combines conventional activated sludge and membrane separation processes. Applications of MBR for spent brine regeneration have been reported in [78]. Despite of the excellent performance in the removal of organic content, fouling remains a main drawback of the process. Numerous strategies have been studied to minimize membrane fouling [95-99]. With the developed control of fouling in the MBR process, MBR could be a promising alternative for spent brine regeneration, particularly for treatment of brine that is heavily polluted with organic compounds.

4.2.3 Ballast Water Treatment

Ballast water treatment technologies can be categorized as physical treatment, chemical treatment, electrochemical treatment, advanced oxidation, and combined treatment (Table 3). Despite the excellent elimination of harmful organisms, these methods still suffer from several drawbacks. For example, UV irradiation requires high energy consumption, the equipment needs to be cleaned periodically, and the lamps are fragile and break easily [100-102]. In addition, UV irradiation is not effective for removal of large organisms and highly depends on the clarity of the water [103]. On the other hand, the electrolysis of ballast water can generate byproducts, especially hydrogen gas (H_2) that has a potential risk of explosion, and the performance is affected by various conditions such as salinity [104]. Oxidizing methods such as chlorination and ozonation can promote the generation of disinfection by products (DBPs) when the disinfectant reacts with chloride and bromide, as presented in [105]. Sonication is effective to remove zooplankton up to 90%, but it is inefficient for the removal of phytoplankton with size < 100 μm [86]. Chemical treatments may also produce various byproducts, while excess chemicals could potentially promote water pollution. Therefore, new alternative methods for treating ballast water are under development, including combined methods to obtain more efficient ballast water treatment.

5 Conclusion

Several approaches have been proposed to provide strategies for brine handling that are oriented at minimizing waste effluent by recovering both brine and water, or to remove pollutant components so it may comply with environmental regulations while being discharged. The dual-purpose desalination and salt production plant is a promising strategy for both rejected brine handling and reducing the total cost of pure water production in a desalination plant. Spent brine regeneration and reuse can be beneficial approaches dealing with spent brine from the ion-exchange regeneration process. Meanwhile, appropriate technologies are required to eliminate harmful organisms from ballast water such as filtration, advanced oxidation, or combined integrative treatments. Furthermore, advanced membrane-based approaches have been summarized and analyzed from an economic point of view as a sustainable alternative for treating various brine effluents.

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