Zero Liquid Discharge System for the Tannery Industry

Subjects: Green & Sustainable Science & Technology

Contributor: Rajamanickam Ricky, Subramanian Shanthakumar, Ganapathy Pattukandan Ganapathy, Fulvia Chiampo

The tannery industry is characterized by the consumption of a large quantity of water, around 30–40 m^3 for processing 1000 kg of hide or skin. This amount becomes wastewater, containing about 300 kg of different chemicals, mainly refractory organic compounds, with high chemical oxygen demand (COD), total dissolved salts (TDS), chromium, and evolution of toxic gases, such as ammonia and sulfides, etc. The remaining tanning chemicals are released as effluent having high resistance against biological degradation, becoming a serious environmental issue. The Zero Liquid Discharge (ZLD) system serves to ensure zero water emission, as well as treatment facilities by recycling, recovery, and reuse of the treated wastewater using advanced cleanup technology. The international scenario shows the implementation of ZLD thanks to pressure from regulatory agencies. The ZLD system consists of a pre-treatment system with conventional physicochemical treatment, tertiary treatment, softening of the treated effluent, reverse osmosis (RO) treatment for desalination, and thermal evaporation of the saline reject from RO to separate the salts. By adopting this system, water consumption is reduced. Moreover, ZLD also becomes effective in disaster mitigation in areas where the tannery industry is a strong economic actor.

Keywords: tannery industry ; wastewater ; environmental pollution ; zero liquid discharge

1. Introduction

The leather industry is an important contributor to the global economy, as the annual global trade reached up to USD 414 billion in 2018, producing a broad range of leather products (footwear, clothing, gloves, handbags, purses, hats, and wristwatch straps) from the rawhide, where 95% of the raw materials are the by-products of meat and dairy industries [1][2]. Asian and European countries are the global leaders in exporting leather products with 48.5% of the worldwide export sale, as plenty of raw material is easily accessible in those nations [3].

The tannery sector is a part of the leather processing industry where the raw leather is converted into finished material. It is considered the most contaminating sector due to the generation of toxic pollutants in every step of the process [4]. Global leather tanneries process 17 million tonnes of hides and skins per year, generate 600 million m^3 of tannery wastewater (TWW), and discharge 350 million m^3 of treated wastewater back into the environment [5]. To convert rawhide into finished leather, the rawhide must undergo several mechanical and chemical processes. It is estimated that 30 L of effluent is generated for the processing of 1 kg of rawhide [6]. The tanning industry utilizes 30 to 40 m^3 of water and about 300 kg of chemicals for processing 1 tonne of rawhide [7]. Only 20% of the raw materials are converted into usable leather products, whereas more than 60% of the raw materials are converted into solid and liquid waste [1].

2. Tanning Process and Related Environmental Issues

Leather manufacturing has four basic stages for processing the raw leather into finished leather, namely, the beam house stage, tanning stage, post-tanning, and finishing stage, each of them based on 10 to 15 operational steps generating solid and liquid waste, as shown in **Figure 1** [8][9]. Raw leather is composed of three layers, namely, the dermis, epidermis, and subcutaneous layer, with the dermis layer consisting of 30–35% of the protein collagen, and the remainder being water and fats [10]. The tanning process involves the reaction between the collagen and chemicals to convert putrescible hide into non-putrescible hide [11]. To increase the hydrothermal stability of the leather, a basification process is employed, where hides soak in tanning liquor to fix the tanning material to the leather [12].

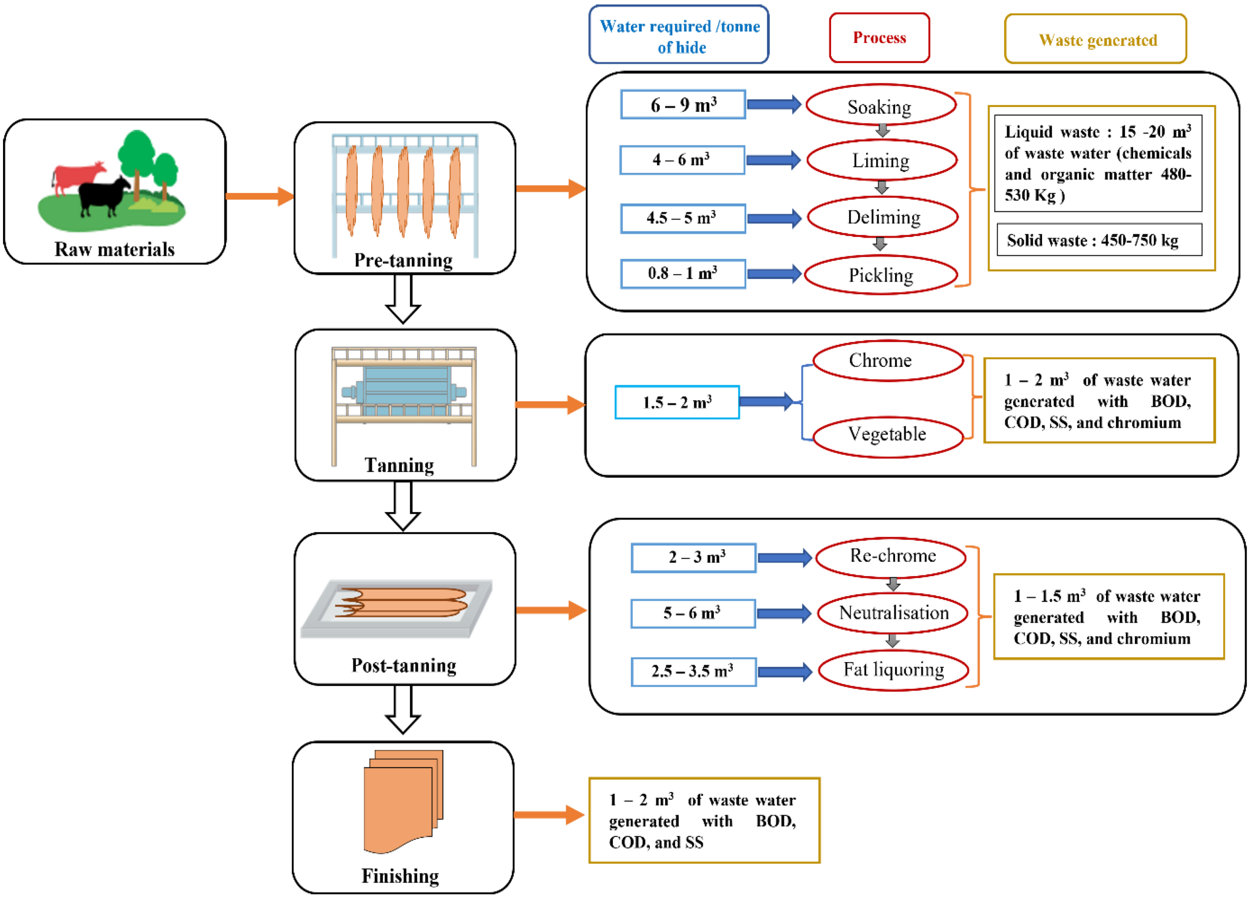

Figure 1. Stages of the leather manufacturing sector with wastewater generated in each of them.

3. Clean Technology Approach in Tanneries

Circular economy practices are an integral part of sustainable development to meet the present needs without compromising the needs of the future. The “6R” principle (reduce, reuse, recycle, recover, redesign, and re-manufacture), which is an evolution of the “3R” principle (reduce, reuse, and recycle), is currently being followed by industries to reach the Sustainable Development Goals by 2030 [13]. In tanneries, waste minimization can be achieved through adopting cleaner technologies, as these processes aim to replace or avoid the usage of harmful chemicals and eliminate the generation of hazardous wastes. Five clean technology approaches can be considered in leather tanning processing:

- High chrome exhaustion: this approach reduces the discharge of chrome by 91% by working without float in the tanning process and replacing formic and sulfuric acid with sulphonic aromatic acid in the process. This approach is 42% more economical than the traditional tanning one [14][15].
- Use of enzymes in the dehairing bath: enzymes are added in the soaking phase to improve the water uptake and to degrade the proteins and fats present in the skin [16]. This approach reduces the processing time.
- Precipitation of chrome: to recover and reuse chrome in spent liquor by raising the pH to minimize the solubility of chromium in the liquor [17].
- Recycling the dehairing bath: instead of discharging it to the treatment plant after a single use, it can be reused after a simple filtration [18].
- Recycling the chrome tanning bath (can reduce chrome use by 20%): reusing the contents in the tanning bath after a simple filtration process [19].

4. Need for Water Recycling in Tanneries

In the tannery industry, water consumption has raised concerns about the availability of freshwater, as the World Bank has estimated that the water demand could increase by over 650% in the next three decades [20]. Water consumption is a major issue in tanneries, and great strides have been made to reduce and recycle water. Water usage can be reduced by 55–58% by using the cleaner technology approach, and recycling the wastewater derived from the pre- and post-tanning process can reduce water consumption by 67% [21]. Minimizing water usage in the leather process can also decrease the treatment cost of the effluents [21]. Treatment of TWW is a multistage process (primary, secondary, and tertiary treatments), where the effluent is treated to reduce the pollution load. In this way, the water can be reused or discharged into the environment after the treatment itself [22]. However, the pollutants, especially the metals, are not completely removed from the wastewater but transferred to disposable sludge. The treated water can be recycled back into the tanneries for non-potable purposes. For the safe disposal of treated wastewater into the environment, it must meet the discharge standards set by the pollution control board [23].

5. Zero Liquid Discharge system

The brine solution discharged from a CETP has always high salinity (TDS = 15–25 g/L) and poses a high risk to health and the environment, as it cannot be used for irrigation or discharged into water recipients [24]. Due to the environmental impacts caused by these pollutants, many countries have laid down strict treatment policies and adopted ZLD for the treatment of TWW [22]. The ZLD system uses a closed water cycle technique so that no water is discharged from the tannery. This eliminates the risk of water contamination by brine discharge and maximizes water usage [25][26]. ZLD can be achieved through the following methods: thermal evaporation, reverse osmosis, electrodialysis, forward osmosis, and membrane distillation. Compared to other technologies, membrane technology is eco-friendly, and it is known to achieve a higher degree of separation without the use of chemicals and thermal energy and has shown to be a promising technology to achieve ZLD in the tannery industry [27]. The ZLD system allows the treatment facility to reclaim and reuse the treated wastewater by employing advanced wastewater treatment technology [28].

5.1. Thermal-Based ZLD Systems

In the early stage of ZLD development, the systems were based on stand-alone thermal processes, where the wastewater generated from the conventional treatment plant was typically evaporated in a brine concentrator followed by a brine crystallizer or evaporation pond, as shown in **Figure 2**. Thermal desalination technologies such as mechanical vapor compression (MVC), multi-effect distillation (MED), and multistage flash (MSF) have been extensively used in seawater desalination plants [29]. MVC is employed in the ZLD systems of tanneries, where the feed water is mixed with brine slurry through the tubes of a heat exchanger, and superheated steam is used to evaporate the brine slurry by heat exchange [30]. Brine concentrators are capable of achieving 98% water recovery with solid concentrations up to 250 g/L [31]. Then, the concentrated brine is fed into a crystallizer for further water recovery by pumping through a submerged heat exchanger [32]. The treated water is collected and recirculated to the tannery sector for reuse. At the end of the ZLD system, salts are produced as by-products. They can be either disposed of through landfills or recovered as valuable salt products [33].

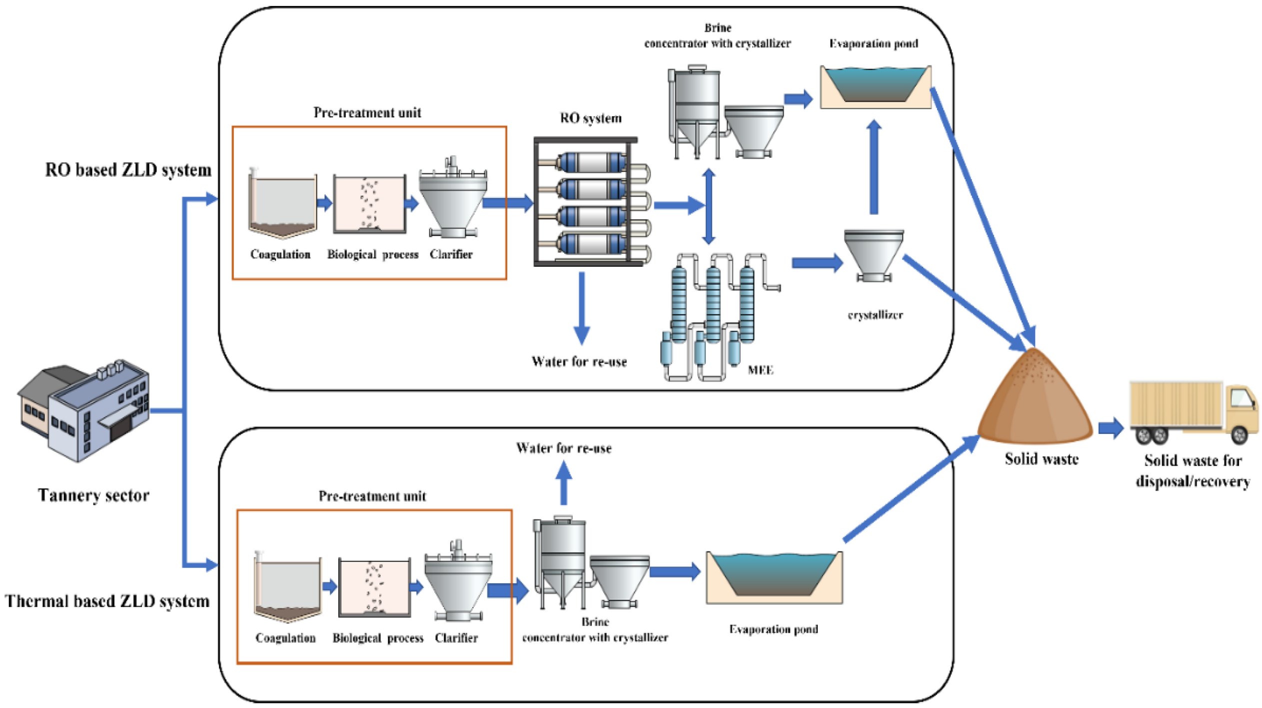

Figure 2. Schematic illustration of thermal- and RO-based ZLD systems.

5.2. RO-Based ZLD Systems

When combined with a conventional thermal-based ZLD system, RO technology can decrease the volume of slurry entering the brine concentrator, thereby reducing energy consumption in MVC. RO eliminates the irreversible losses associated with evaporation and condensation in thermal processes [34]. This membrane section is located before the MVC brine concentrator to preconcentrate the feedwater so that it can reduce the load on the concentrator, as shown in **Figure 2**. RO uses around 2 kWh/m^3 of wastewater, which is much lower than the consumption of the combination MVC concentrator + crystallizer [35].

6. Critical Assessment of ZLD Economics

The ZLD system is employed to ensure and enable the treatment facility to recycle, recover, and reuse treated wastewater. Installation of the ZLD system requires substantial capital costs and poses a great challenge technically and financially for tanneries. When ZLD systems for tanneries were installed for the first time, operation and maintenance costs were 7–10 times higher than the conventional effluent treatment plant [36][37]. Accumulation of solid waste from the system is one of the drawbacks of the ZLD system as it offers no re-use potential, being a mixture of salts. Despite benefits including yielding freshwater, the cost is still prohibitively high [38], even if the reduction in RO reject can drastically reduce the operational cost [39].

The energy required by a RO system is greatly utilized for pumping. The power consumption of the RO section is about 50% of the total treatment costs. The other costs are 37% for fixed costs, which include insurance and capital investment amortization, 7% for maintenance, 5% for membrane replacement, and 1% for labor and consumable chemicals [40]. Membrane pretreatment (MF, UF, and NF) of wastewater to feed to RO can increase the life of the RO membrane, reducing the cost of membrane replacement [41]. This operation has become mandatory for the sustainable approach in the ZLD system. Bench-scale and pilot-scale studies are being conducted to reduce the cost of implementing ZLD technology [42].

When ZLD is applied in tanneries, the method of action for dealing with the RO reject water must be specified. Solar evaporation pond is a traditional method that has been employed, but the land required for the pond system is high and the average evaporation rate is estimated to be 2.54–10.16 mm of water/day [43]. It is an effective method, especially in countries with warm weather conditions, as it can increase the evaporation rate. A sprinkler system in the pond can accelerate the evaporation rate. The evaporation ponds must be sealed with liners to avoid groundwater contamination and soil salinity [44]. The drawback is that water is not recovered, and the system is not effective during rains. Installing a multiple-effect evaporator can overcome this drawback. This technique allows the recovery of the evaporated water as condensate, with its recirculation into the industry for reuse [45].

The ZLD process has considerable capital and operating costs, but the system recovers 75% of the water and recycles it back for reuse, thus reducing the demand for freshwater [46]. Because of the impacts of the saline water on the environment, evaporation of this saline reject water to dryness is the only possible approach to disposal. This process of converting the salt liquor into solid waste forces additional charges on the ZLD system. The generated solid waste is composed of a mixture of salts such as chlorides, sulfates, carbonates, and nitrates, which raises the disposal problem for the tanneries, as the evaporated salts cannot be used for any other purposes [47]. The salt disposal would bring in additional costs that would make the whole ZLD system much more cumbersome. The capital investment and the operation cost challenge the sustainability of the whole system.

References

1. Sivaram, N.M.; Barik, D. Toxic waste from leather industries. In Energy from Toxic Organic Waste for Heat and Power Generation; Woodhead Publishing: Cambridge, UK, 2018; pp. 55–67. ISBN 9780081025284.
2. Saran, S.; Chib, S.; Saxena, R.K. Biotechnology of leather: An alternative to conventional leather processing. A Handb. High Value Ferment. Prod. Hum. Welf. 2019, 2, 23–47.
3. Saranya, D.; Shanthakumar, S. Opportunities for phycoremediation approach in tannery effluent: A treatment perspective. Environ. Prog. Sustain. Energy 2019, 38, e13078.
4. Suman, H.; Sangal, V.K.; Vashishtha, M. Treatment of tannery industry effluent by electrochemical methods: A review. Mater. Today Proc. 2021, 47, 1438–1444.

5. Rajamani, S. Sustainable Environmental Technologies Including Water Recovery for Reuse from Tannery and Industrial Wastewater–Indian and Asian Scenario. Ann. Univ. Oradea Fascicle Text. Oradea Rom. 2017, 173–179.
6. Doble, M.; Kruthiventi, A.K. Industrial Examples. In Green Chemistry and Engineering; Academic Press: Burlington, ON, Canada, 2007; pp. 245–296. ISBN 978-0-12-372532-5.
7. Lofrano, G.; Meriç, S.; Zengin, G.E.; Orhon, D. Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review. Sci. Total Environ. 2013, 461–462, 265–281.
8. Famielec, S. Chromium concentrate recovery from solid tannery waste in a thermal process. Materials 2020, 13, 1533.
9. Sundar, V.J.; Ramesh, R.; Rao, P.S.; Saravanan, P.; Sridharnath, B.; Muralidharan, C. Water management in leather industry. J. Sci. Ind. Res. 2001, 60, 443–450.
10. Sivakumar, V.; Swaminathan, G.; Rao, P.G.; Ramasami, T. Influence of ultrasound on diffusion through skin/leather matrix. Chem. Eng. Process. Process Intensif. 2008, 47, 2076–2083.
11. Thazeem, B.; Umesh, M.; Mani, V.M.; Beryl, G.P.; Preethi, K. Biotransformation of bovine tannery fleshing into utilizable product with multifunctionalities. Biocatal. Biotransformation 2021, 39, 81–99.
12. Saravanabhavan, S.; Thanikaivelan, P.; Rao, J.R.; Nair, B.U.; Ramasami, T. Reversing the conventional leather processing sequence for cleaner leather production. Environ. Sci. Technol. 2006, 40, 1069–1075.
13. Karuppiah, K.; Sankaranarayanan, B.; Ali, S.M.; Jabbour, C.J.C.; Bhalaji, R.K.A. Inhibitors to circular economy practices in the leather industry using an integrated approach: Implications for sustainable development goals in emerging economies. Sustain. Prod. Consum. 2021, 27, 1554–1568.
14. Morera, J.M.; Bacardit, A.; Ollé, L.; Bartolí, E.; Borràs, M.D. Minimization of the environmental impact of chrome tanning: A new process with high chrome exhaustion. Chemosphere 2007, 69, 1728–1733.
15. Bacardit, A.; Morera, J.M.; Ollé, L.; Bartolí, E.; Dolors Borràs, M. High chrome exhaustion in a non-float tanning process using a sulphonic aromatic acid. Chemosphere 2008, 73, 820–824.
16. Singhania, R.R.; Patel, A.K.; Thomas, L.; Goswami, M.; Giri, B.S.; Pandey, A. Industrial Enzymes. In Industrial Biorefineries and White Biotechnology; Pandey, A., Höfer, R., Taherzadeh, M., Nampoothiri, K.M., Larroche, C., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 473–497. ISBN 9780444634535.
17. Kanagaraj, J.; Chandra Babu, N.K.; Mandal, A.B. Recovery and reuse of chromium from chrome tanning waste water aiming towards zero discharge of pollution. J. Clean. Prod. 2008, 16, 1807–1813.
18. Collivignarelli, C.; Barducci, G. Waste recovery from the tanning industry. Waste Manag. Res. 1984, 2, 265–278.
19. Blackman, A. Adoption of Clean Leather-Tanning Technologies in Mexico. Discussion Papers 10881, Resources for the Future; Washington, DC, USA, 2005; DP 05-38; Available online: https://ageconsearch.umn.edu/record/10881 (accessed on 22 May 2022).
20. Molden, D.; Amarasinghe, U.; Hussain, I. Water for Rural Development—Background Paper on Water for Rural Development; International Water Management Institute: Anand, India, 2001; Volume 32, ISBN 9290904593.
21. Raghava Rao, J.; Chandrababu, N.K.; Muralidharan, C.; Nair, B.U.; Rao, P.G.; Ramasami, T. Recouping the wastewater: A way forward for cleaner leather processing. J. Clean. Prod. 2003, 11, 591–599.
22. Zhao, C.; Chen, W. A review for tannery wastewater treatment: Some thoughts under stricter discharge requirements. Environ. Sci. Pollut. Res. 2019, 26, 26102–26111.
23. Ahamed, M.I.N.; Kashif, P.M. Safety Disposal of Tannery Effluent Sludge: Challenges to Researchers- a Review. Int. J. Pharm. Sci. Res. 2014, 5, 733–736.
24. Sinha, S.; Singh, S.; Mallick, S. Comparative growth response of two varieties of Vigna radiata L. (var. PDM 54 and var. NM 1) grown on different tannery sludge applications: Efects of treated wastewater and ground water used for irrigation. Environ. Geochem. Health 2008, 30, 407–422.
25. Suthanthararajan, R.; Ravindranath, E.; Chitra, K.; Umamaheswari, B.; Ramesh, T.; Rajamani, S. Membrane application for recovery and reuse of water from treated tannery wastewater. Desalination 2004, 164, 151–156.
26. Byers, B. Zero discharge: A systematic approach to water reuse. Chem. Eng. 1995, 102, 96.
27. Yang, F.; Huang, Z.; Huang, J.; Wu, C.; Zhou, R.; Jin, Y. Tanning wastewater treatment by ultrafiltration: Process efficiency and fouling behavior. Membranes 2021, 11, 461.
28. Liang, Y.; Lin, X.; Kong, X.; Duan, Q.; Wang, P.; Mei, X.; Ma, J. Making waves: Zero liquid discharge for sustainable industrial effluent management. Water 2021, 13, 2852.
29. Qiblawey, H.M.; Banat, F. Solar thermal desalination technologies. Desalination 2008, 220, 633–644.

30. Bostjancic, J.; Ludlum, R. Getting to Zero Discharge: How to Recycle That Last Bit of Really Bad Wastewater A Brief History of Evaporation. In Proceedings of the International Water Conference, Engineers Society of Western Pennsylvania, West Chester, PA, USA, 21–24 April 1996; Volume 57, pp. 290–295.
31. Yaqub, M.; Lee, W. Zero-liquid discharge (ZLD) technology for resource recovery from wastewater: A review. Sci. Total Environ. 2019, 681, 551–563.
32. Giwa, A.; Dufour, V.; Al Marzooqi, F.; Al Kaabi, M.; Hasan, S.W. Brine management methods: Recent innovations and current status. Desalination 2017, 407, 1–23.
33. Boopathy, R.; Karthikeyan, S.; Mandal, A.B.; Sekaran, G. Characterisation and recovery of sodium chloride from salt-laden solid waste generated from leather industry. Clean Technol. Environ. Policy 2013, 15, 117–124.
34. Al-Karaghouli, A.; Kazmerski, L.L. Energy consumption and water production cost of conventional and renewable-energy-powered desalination processes. Renew. Sustain. Energy Rev. 2013, 24, 343–356.
35. Elimelech, M.; Phillip, W.A. The future of seawater desalination: Energy, technology, and the environment. Science 2011, 333, 712–717.
36. Pérez-González, A.; Urtiaga, A.M.; Ibáñez, R.; Ortiz, I. State of the art and review on the treatment technologies of water reverse osmosis concentrates. Water Res. 2012, 46, 267–283.
37. Almulla, A.; Eid, M.; Côté, P.; Coburn, J. Developments in high recovery brackish water desalination plants as part of the solution yp water quantity problems. Desalination 2003, 153, 237–243.
38. Li, W.; Krantz, W.B.; Cornelissen, E.R.; Post, J.W.; Verliefde, A.R.D.; Tang, C.Y. A novel hybrid process of reverse electrodialysis and reverse osmosis for low energy seawater desalination and brine management. Appl. Energy 2013, 104, 592–602.
39. Robertson, A.; Nghiem, L.D. Treatment of High TDS Liquid Waste: Is Zero Liquid Discharge Feasible? J. Water Sustain. 2011, 1, 1–11.
40. Younos, T. The Economics of Desalination. J. Contemp. Water Res. Educ. 2009, 132, 39–45.
41. Mickley, M.C. Membrane Concentrate Disposal: Practices and Regulation; US Department of the Interior, Bureau of Reclamation, Technical Service: Denver, CO, USA, 2006; Volume 123, ISBN 1856173895.
42. Loganathan, K.; Chelme-Ayala, P.; Gamal El-Din, M. Pilot-scale study on the treatment of basal aquifer water using ultrafiltration, reverse osmosis and evaporation/crystallization to achieve zero-liquid discharge. J. Environ. Manag. 2016, 165, 213–223.
43. Pancharatnam, S. Transient Behavior of a Solar Pond and Prediction of Evaporation Rates. Ind. Eng. Chem. Process Des. Dev. 1972, 11, 287–292.
44. Ahmed, M.; Shayya, W.H.; Hoey, D.; Mahendran, A.; Morris, R.; Al-Handaly, J. Use of evaporation ponds for brine disposal in desalination plants. Desalination 2000, 130, 155–168.
45. Rajkumar, R.; Sathish, S.; Senthilkumar, P. Studies on enhancing the efficiency of ZLD plant for tannery effluent by implementing Low-Cost ambient air evaporator system. Rasayan J. Chem. 2018, 11, 13–17.
46. Martínez, J.; León, E.; Baena-Moreno, F.M.; Rodríguez-Galán, M.; Arroyo-Torralvo, F.; Vilches, L.F. Techno-economic analysis of a membrane-hybrid process as a novel low-energy alternative for zero liquid discharge systems. Energy Convers. Manag. 2020, 211, 112783.
47. Buljan, J.; Emmanuel, K.V.; Viswanathan, M.; Bosnić, M.; Král, I. Analysis of flow and energy aspects of Zero Liquid Discharge (ZLD) technology in treatment of tannery effluents in Tamil Nadu, India. In Proceedings of the 34th IULTCS Congress: Science and Technology for Sustainability of Leather, Chennai, India, 6 February 2017; pp. 244–259.