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Economic Analysis of an Innovative Scheme for the Treatment of Produced Waters

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During the crude oil extraction processes, for each barrel of oil turns out an equivalent of 3 barrels of wastewaters on average. These wastes are known as Produced Waters (PWs) and their dramatic impact on the environment has attracted the attention of researchers in order to find an economic and efficient method for their treatment. Dealing with PWs is not easy: the long exposure with oil increases their hydrocarbon fraction, while the contact with the underground wells increases their concentration in salts and minerals. The direct discharge of PWs into the sea is obviously not allowed by law and PWs are usually re-injected into the well.

The present work deals with a novel and innovative treatment chain (including assisted reverse electrodialysis (ARED) as dilution step) able to reduce both the salinity and organic content of PWs. The innovative scheme includes an ultrafiltration unit as pre-treatment, upstream an ARED unit for the PW dilution. Once the salinity level has been reduced down to a value affordable for a bioremediation step, PWs are sent to a bio-reactor, where the organic compounds are digested. Finally, a reverse osmosis unit is used to recover water from the treated PWs and to recycle it as diluted stream in the ARED unit. A techno-economic model was purposely developed in the present work to assess the economic feasibility of the proposed scheme. Preliminary results suggest that the treatment costs are lower than 5 € $m^{-3}{}_{PW}$ and fully competitive with current PWs treatment technologies.

1. Introduction

Produced waters (PWs) is one of the main liquid wastes of oil and gas production. Generally, PWs are wastewaters including the formation water (water caught for millions of years in strictly contact with the reservoir) and the water that is used during the drilling processes to increase, when necessary, the oil recovery and the process safety. The ratio between the drilled oil (or gas) and the generated PWs can vary from zero to more than 50, being this ratio particularly affected by the plant age and by the remaining quantity of oil (Neff et al., 2011). It was estimated global PWs volume in 2009 was more than 11.2 million of m^3 (Al-Ghouti et al., 2019).

Due to the strictly contact with oil and gas, PWs are polluted by hydrocarbons. Also, PWs are salty as they are kept inside the impermeable layers of rock in the subsoil (Igunnu and Chen, 2014). Several strategies are used to deal with these wastewaters, such as the recycle like the enhanced oil recovery technique, or the reuse for industrial or agricultural purpose, or lastly, the direct disposal. If the first two options foresee a way to resolve and trying to valorise a waste, the third method, mostly consist in the direct injection in the underground, i.e. into non-operative well (Veil, 2011). Although the injection is the most common way for the disposal of PWs, this practise is not always feasible like in the offshore site, besides the fact that is not appreciated by social communities which considered it as unfriendly and unsustainable.

Different options are available for the treatment of these wastewaters. The treatment techniques are categorized on the base of the process used, so they are distinguished in physical, chemical and biological processes *(Jiménez et al., 2018)*. Physical and chemical methods are typically quite expensive. Bioremediation techniques could be an effective and affordable option for the removal of the organic compounds, but the high salinity of

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the PWs inhibit bacteria growth and metabolism. Different strategies have been proposed in literature for the salt reduction: most of them are thermal-based methods, thus being energy-demanding and often very costly. Recently, membrane processes as Salinity Gradient Power (SGP) technologies have been proposed as a possible alternative.

Reverse Electrodialysis (RED) is a technology able to convert directly the salinity difference between two solutions into electric energy, thus providing, as additional benefit, the reduction of the high salinity solution (i.e., the PW). The desalination of PWs may be boosted by adding an external power supply to the unit, which increases the flux of ions in the same direction of the current, i.e., from the concentrate solution towards the diluted one: the resulting technology is known as Assisted Reverse Electrodialysis (ARED).

Cosenza et al. 2022 have already demonstrated the technical feasibility of using a RED stack fed by PWs to produce electrical energy. Furthermore, a semi empirical model was also calibrated and validated for the prediction of RED and ARED units dealing with PWs: it showed the convenience of adopting an ARED process (Campisi et al., 2023) for desalination purposes. In the present work, Authors propose an innovative scheme for the treatment and valorisation of PWs by combining membrane-separation processes with bioremediation.

2. Process description and mathematical model

A Block Flow Diagram (BFD) is reported in Figure 1 showing the main units and streams of the treatment chain.

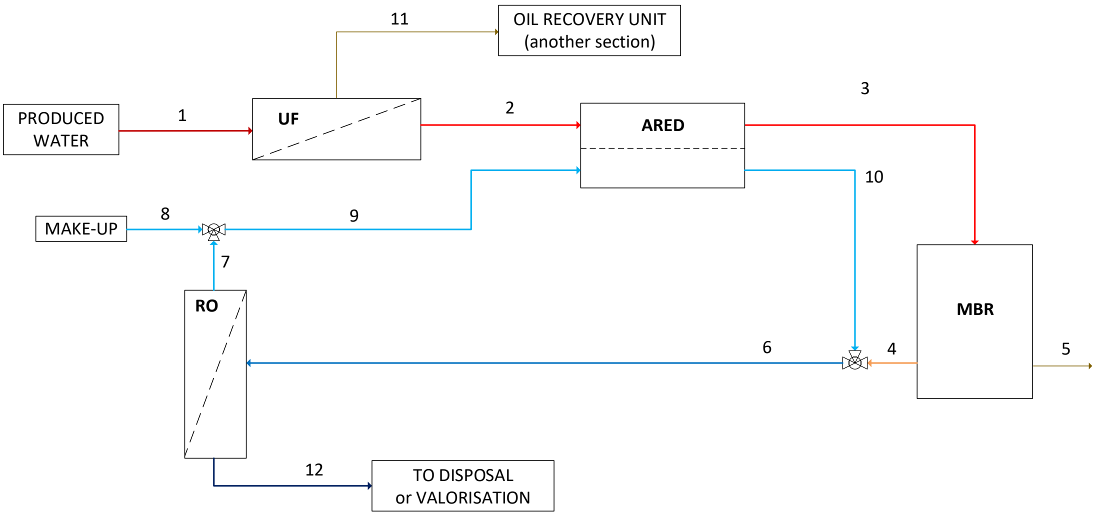

Figure 1: Block flow diagram of the treatment chain proposed.

Firstly, the PWs are filtered in an ultrafiltration (UF) unit, where it is assumed that only the 95% can be recovered from the process as filtered PWs (stream 2). UF uses ceramic membranes (chosen for their chemical stability and physical resistance) to filter the PWs and remove the major organic compounds, which are collected as retentate (stream 11). The UF retentate should be treated by a suitable process: it typically is the crude oil recovery section already existing in the plant. The UF permeate (i.e., the filtered PWs) is sent to the ARED unit where it is mixed (without a direct contact) with a diluted solution (stream 9). The purpose of the ARED unit is to reduce the salinity before the downstream bioremediation step (Pendashteh et al., 2012) to a target concentration of 20 g L^{-1}, which was found compatible with autochthone bacteria metabolism. The biological reactor selected for the reduction of organic compounds is a MBR (Membrane Bio Reactor): it allows treating a higher volume, with good efficiency and low energy consumption (Schneider et al., 2011). Furthermore, this kind of bioreactor was already suggested as method to deal with oily and saline wastewaters (Di Bella et al., 2015). For the MBR unit it is assumed that the unit is fully capable of reducing the PWs organic compounds to the minimum value accepted by the local legislation. Conversely, salinity is not modified by the biological action. Similarly, the diluted solution used for the ARED unit comes out more concentrated, with a concentration corresponding to the amount of removed salt. The two streams (the diluted exiting ARED and the PWs after the biological treatment, stream 4 and 10) are mixed and sent to a Reverse Osmosis (RO) unit to reduce the salt concentration and re-use the permeate of the process as diluted stream in the ARED unit. A make-up stream of process water (stream 8) is inserted before the ARED to close the mass balance of the diluted circuit. Concerning the retentate (stream 12), since no downstream processes are considered in the present work, it should be regarded as a liquid waste for the plant. However, this concentrated stream may result particularly rich in valuable minerals and precious metals and may be sent to a suitable downstream valorization section (e.g. including ion exchange resins and crystallizers).

2.1 Techno-economic model and assumptions

The whole plant is simulated with a techno-economic model on Excel and VBA. The technical model is used to predict the behavior of each unit and the corresponding streams of the plant in terms of flow rate and salt concentration. Table 1 summarizes the assumptions for each unit of the treatment chain.

Table 1: Summary of the assumptions of the main units of the PWs treatment chain

Unit	Assumption
Ultrafiltration (UF)	Ceramic membranes are used in UF modules. The permeate (stream 2) does not change its salinity and the UF is only able to retain the highest weight organic compounds. A 95 % recovery is assumed and the retentate (stream 13) of the unit is sent to an oil recovery unit typically present in the situ. The economic model estimate both capital and operative expenditure according to Nguyen and Yoshikawa, 2019. In order to evaluate some of the costs a flux of 30 L m^{-2} h^{-1} (deduced by Baker, 2000, Chapter 6) and a feed pressure of 5 bar are assumed.
Assisted reverse electrodialysis (ARED)	The technical model calibrated with real PWs, and the economic aspects and correlations used in this work are minutely described in Campisi et al., 2023. The cost of the ARED membranes is chosen as a possible future cost achievable with a future suitable economy of scale making the technology market competitive with other industrial applications.
Membrane bio-reactor (MBR)	The MBR is assumed ideal. The purge flow (stream 5) is assumed negligible. The costs (function of the scale, i.e. stream 3) are estimated according to Iglesias et al., 2017.
Reverse osmosis (RO)	The RO unit is constituted by 7 elements in series, it is assumed that the feed inlet is constituted by a concentration of NaCl only. Further details are described in Table 3. The technical model of the unit is reported in La Cerva et al., 2019; the economic model is in accordance to Park et al., 2017.

The integrated model is able to solve the mass balances, predict the output and the behavior of the ARED and RO processes and calculate the costs of the different units, i.e., both fixed capital investment (FCI, €) and operative expenditure (Opex, € $year^{-1}$). The Opex depends on the day-to-day operation of the plant such as chemicals, electricity, etc., whilst the FCI is cost needed to purchase the equipment and build the plant. For a better comparison of these two different costs, the FCI is annualized considering a discount rate *r* and *t* years of plant lifetime, according to eq. 1.

$$\mathrm{Acapex} = \frac{\mathrm{r(1+r)^t}}{\mathrm{(1+r)^t - 1}}\mathrm{FCI} \tag{1}$$

More in general, for each unit both Acapex and Opex are calculated: the main cost items and the economic parameters needed to do that are presented in Table 2.

Table 2: Main costs of the unit and the plant

Economic Parameter	Value		Economic Parameter	Value	
Plant lifetime, t	20	year	ARED membrane lifetime	4	year
Discount rate, r	3	%	ARED spacers cost	5	€ m^{-2}_{IEMs}
Working hour per year	8000	h $year^{-1}$	ARED casing cost	2	€ m^{-2}_{IEMs}
Pump efficiency	80	%	ARED electrode cost	500	€ m^{-2}
Electricity cost	0.12	€ kWh^{-1}	ARED labour cost	20	% of ARED direct costs
Water cost	0.3	€ m^{-3}_{W}	RO membrane cost	10	€ m^{-2}
UF membrane cost	200	€ m^{-2}	Construction year	2030	-
ARED membrane cost	20	€ m^{-2}_{IEMs}	Plant located region	Southern European countries	

Finally, the total plant cost C_{tot} is the sum of the annualized capital costs and the operative expenditure. Notably, C_{tot} is a specific cost as it is normalized (eq. 2) to the plant size, i.e., the cubic meters of PWs treated by the plant.

$$\mathrm{C_{tot}} = \frac{\mathrm{Acapex + Opex}}{\mathrm{Plant\ size\ [m^3_{PW}\ year^{-1}]}} \tag{2}$$

2.2 Case scenario and technical data

The techno-economic model includes different possibilities of choice, varying from the plant scale to the RO unit pressure, from the voltage applied in ARED to the cost of fresh water make up.

As a starting point, a scale of 10.5 $m^3 h^{-1}$ for the plant was considered. This flow, after the preliminary UF unit, is divided up into 5 stacks of ARED. Each deals with a concentrate flow rate of 2 $m^3 h^{-1}$; the corresponding dilute solution flow rate is assumed equal to twice the concentrate one (i.e. 4 $m^3 h^{-1}$). The different flow rates imply a difference in the velocity, that can influence the pressure drops of the system (because the channel with the higher flow can push against the adjacent channel), for this reason different spacers were assumed for the concentrated and diluted channels, respectively 300 e 500 µm. The main operating parameter of RO is the operating pressure, that is calibrated depending on the feed concentration and aiming at the reduction of the water make-up stream. The main input and fixed parameters are shown in the following table:

Table 3: Main input parameters and fixed values

Assisted Reverse Electrodialysis, ARED, stack			Reverse Osmosis, RO, unit		
Data	Value		Data	Value	
Number of cell pair, N_{cp}	500	-	Module SW30XHR-440i[1]		
Stack width, b	1	m	Area of membranes	41	m^2
Stack Length, L	1	m	Length of module	1.016	m
Stream 2 velocity, v_H	0.45	cm s^{-1}	Spacer thickness	0.7112	mm
Stream 2 flow rate	2	$m^3 h^{-1}$	Max Feed flow rate	15.49	$m^3 h^{-1}$
Stream 2 spacer thickness, δ_H	300	µm	Max Permeate flow rate	1.320	$m^3 h^{-1}$
Stream 9 velocity, v_L	0.54	cm s^{-1}	Max feed pressure	82.74	bar
Stream 9 flow rate	4	$m^3 h^{-1}$			
Stream 9 spacer thickness, δ_L	500	µm	[1] Data provided by Wave software		

3. Results and Discussion

The plant presents a plethora of scenario variables and input parameters. However, there are two key variables in the process: (i) the voltage applied to the ARED unit which determines the salinity of the PW exiting the unit and (ii) the RO feed pressure which defines how much water can be recovered and recycled to the ARED with a decrease of the water make-up. In some circumstances (such as different flow rates or lower PWs concentration) it may also be possible to obtain an exceed of process water, that could be sold or reuse in another part of the plant situ.

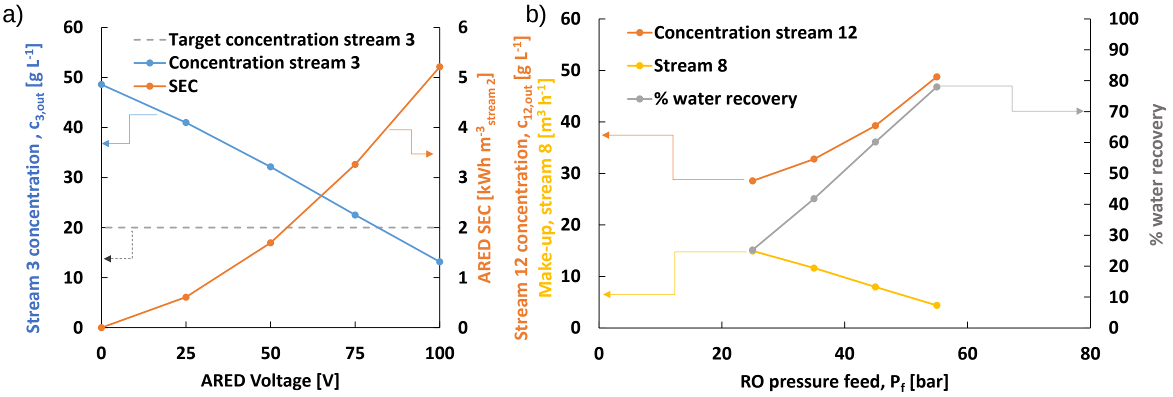

Figure 2: Technical analysis of the PWs treatment plant varying the voltage of ARED unit and the pressure of the RO feed. a) Stream 3 concentration, target concentration of 20 g L^{-1} and specific energy consumption (SEC) of the ARED unit; b) Water recovery, flow rate of make-up stream and concentration of stream 12 versus the RO pressure feed.

A technical analysis is presented in Figure 2. There is a minimum voltage value required to achieve the concentration goal of 20 g L^{-1} at the outlet of the ARED unit (the maximum allowed in the bioreactor), and this is about 80 V, with a corresponding specific energy consumption (SEC) of 3.7 kWh $m^{-3}{}_{stream2}$ defined as the power required per m^3 of PW entering into ARED, as shown in Figure 2.a. Concerning RO feed pressure (Figure 2.b), the higher the pressure, the larger the water savings in the treatment chain: this might be a matter of crucial importance in all those places where the water is not easily available. When RO pressure is low, the water demand amounts to 14.95 m^3_w per hour. This quantity can be reduced by increasing the RO pressure, corresponding to a water recovery of 78 %, defined as the ratio of stream 7 to stream 9. It should be noted that as the pressure increases, the concentration of retentate increases as well, reaching values even close to 50 g L^{-1}. A high concentration of the RO retentate could be a perfect advantage for minerals and metals recovery when a valorisation section is downstream coupled to the chain. Conversely, if a disposal into the sea is foreseen, the retentate concentration $c_{12,out}$ should be maintained to a value minor or equal to the sea water concentration (about 35 g L^{-1}) in order to avoid the sea desertification phenomenon (Ramasamy, 2020).

Based on Figure 2 results, the operative conditions adopted for the cost analysis consider a voltage of 80 V for the ARED unit and an operative pressure of 35 bar for the stream 6 (i.e., the RO feed). The corresponding total costs of the plant are shown in Figure 3 where three different plant sizes are considered: a relatively little plant with a size of 10.5 m$^3_{PW}$ h^{-1}, a medium one of 52.6 m$^3_{PW}$ h^{-1} and a large plant with a size of 105.3 m$^3_{PW}$ h^{-1}.

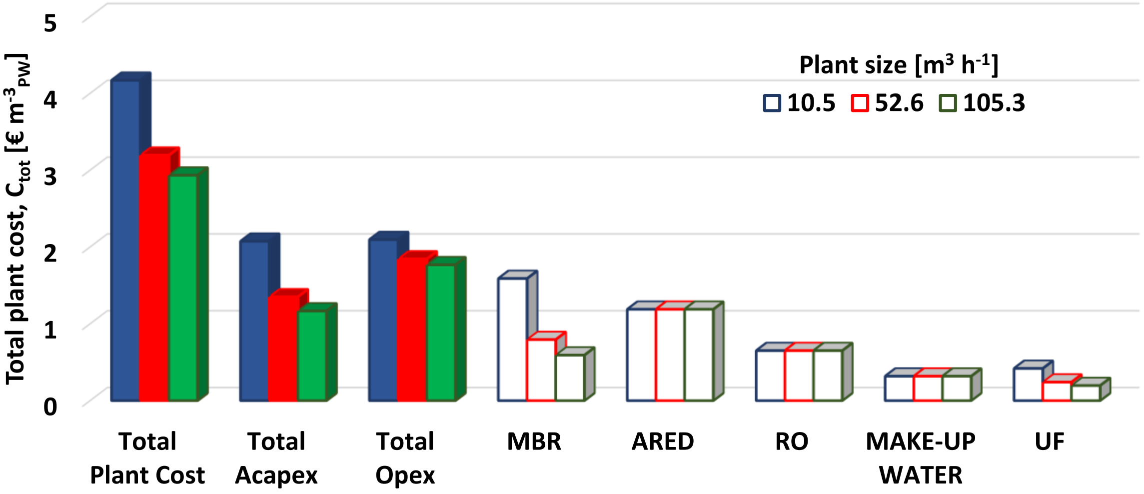

Figure 3: Total costs of the plant and of the singular units for three different plant size.

The larger the plant size, the lower the total cost of the plant, as expected: it ranges from 4.17 to 2.93 € m$^{-3}_{PW}$. This variation is mainly due to the biological unit which is more sensible to the scale-up. Conversely, ARED and RO being modular technologies have a cost poorly dependent on size. Capital costs exhibit a stronger dependence on size than operating costs. This different dependence leads operating costs to be prominent only at large plant sizes. The preliminary techno-economic analysis here presented shows that the proposed treatment chain exhibit costs being competitive with the typical treatment costs of PWs. Notably, no optimization has been performed, thus showing that there is still room for improvement aiming to find the best configuration between technical and economic features. Ad hoc experimental analysis are also needed to describe in detail the composition and features of all the streams involved in the process.

4. Conclusions

The large volumes of PWs produced nowadays has required a way to deal with them, either the re-use, the recycle or the direct disposal. In this last scenario, a preliminary treatment is necessary to avoid dramatic environmental impacts. In this work, a novel scheme for the their treatment is presented. It mainly consists of a bioremediation step downstream a suitable process devoted to reducing the PWs high salinity. A techno-economic model is implemented to estimate the main technical data (e.g., the flow rate of the streams or their concentration) and to predict the cost of the single units and of the overall plant.

Although there are many scenario variables and input parameters, the applied voltage in the ARED stack and the feed pressure of the RO unit are the two key variables. The first defines the outlet concentration of the PWs exiting the ARED unit. Being this a constrain (i.e. 20 g L^{-1}), a minimum voltage of 80 V is found necessary to achieve this concentration target. The choice of the second variable (the pressure) depends on different conditions: on the one hand, the higher the pressure, the higher the RO cost and the less the water demand of the plant; on the other hand, the higher the pressure, the larger the retentate concentration and the seawater desertification effect). A pressure of 35 is a good compromise, because the outlet concentration results equal to the seawater concentration, thus allowing the disposal into the sea. However, downstream valorisation processes could be a fair possibility, and in that case, higher RO pressure would be an advantage. Finally, a total plant cost of 4.17 € $m^{-3}{}_{PW}$ was found for a small plant size. Scale-up can lead to a reduction of this cost up to a value of 2.93 € $m^{-3}{}_{PW}$, thus showing how much this plant could be a reasonable and feasible PWs treatment.

References

Al-Ghouti, M.A., Al-Kaabi, M.A., Ashfaq, M.Y., Da'na, D.A., 2019. Produced water characteristics, treatment and reuse: A review. Journal of Water Process Engineering 28, 222–239. doi.org/10.1016/j.jwpe.2019.02.001

Baker, R.W., 2000. Membrane technology and applications, McGraw-Hill professional engineering. McGraw-Hill, New York.

Campisi, G., Cosenza, A., Giacalone, F., Randazzo, S., Tamburini, A., Micale, G., 2023. Desalination of oilfield produced waters via reverse electrodialysis: A techno-economical assessment. Desalination 548, 116289. doi.org/10.1016/j.desal.2022.116289

Cosenza, A., Campisi, G., Giacalone, F., Randazzo, S., Cipollina, A., Tamburini, A., Micale, G., 2022. Power Production from Produced Waters via Reverse Electrodialysis: A Preliminary Assessment. Energies 15, 4177. doi.org/10.3390/en15114177

Di Bella, G., Di Prima, N., Di Trapani, D., Freni, G., Giustra, M.G., Torregrossa, M., Viviani, G., 2015. Performance of membrane bioreactor (MBR) systems for the treatment of shipboard slops: Assessment of hydrocarbon biodegradation and biomass activity under salinity variation. Journal of Hazardous Materials 300, 765–778. doi.org/10.1016/j.jhazmat.2015.08.021

Iglesias, R., Simón, P., Moragas, L., Arce, A., Rodriguez-Roda, I., 2017. Cost comparison of full-scale water reclamation technologies with an emphasis on membrane bioreactors. Water Science and Technology 75, 2562–2570. doi.org/10.2166/wst.2017.132

Igunnu, E.T., Chen, G.Z., 2014. Produced water treatment technologies. Int. J. Low-Carbon Tech. 9, 157–177. doi.org/10.1093/ijlct/cts049

Jiménez, S., Micó, M.M., Arnaldos, M., Medina, F., Contreras, S., 2018. State of the art of produced water treatment. Chemosphere 192, 186–208. doi.org/10.1016/j.chemosphere.2017.10.139

La Cerva, M., Gurreri, L., Cipollina, A., Tamburini, A., Ciofalo, M., Micale, G., 2019. Modelling and cost analysis of hybrid systems for seawater desalination: Electromembrane pre-treatments for Reverse Osmosis. Desalination 467, 175–195. doi.org/10.1016/j.desal.2019.06.010

Neff, J., Lee, K., DeBlois, E.M., 2011. Produced Water: Overview of Composition, Fates, and Effects, in: Lee, K., Neff, J. (Eds.), Produced Water. Springer New York, New York, NY, pp. 3–54. doi.org/10.1007/978-1-4614-0046-2_1

Nguyen, T.-A., Yoshikawa, S., 2019. Modeling and Economic Optimization of the Membrane Module for Ultrafiltration of Protein Solution Using a Genetic Algorithm. Processes 8, 4. doi.org/10.3390/pr8010004

Park, K., Kim, D.Y., Yang, D.R., 2017. Cost-based feasibility study and sensitivity analysis of a new draw solution assisted reverse osmosis (DSARO) process for seawater desalination. Desalination 422, 182–193. doi.org/10.1016/j.desal.2017.08.026

Pendashteh, A.R., Abdullah, L.C., Fakhru'l-Razi, A., Madaeni, S.S., Zainal Abidin, Z., Awang Biak, D.R., 2012. Evaluation of membrane bioreactor for hypersaline oily wastewater treatment. Process Safety and Environmental Protection 90, 45–55. doi.org/10.1016/j.psep.2011.07.006

Ramasamy, B., 2020. Short Review of Salt Recovery from Reverse Osmosis Rejects, in: Cengiz Çinku, M., Karabulut, S. (Eds.), Salt in the Earth. IntechOpen. doi.org/10.5772/intechopen.88716

Schneider, E.E., Cerqueira, A.C.F.P., Dezotti, M., 2011. MBBR evaluation for oil refinery wastewater treatment, with post-ozonation and BAC, for wastewater reuse. Water Science and Technology 63, 143–148. doi.org/10.2166/wst.2011.024

Veil, J.A., 2011. Produced Water Management Options and Technologies, in: Lee, K., Neff, J. (Eds.), Produced Water. Springer New York, New York, NY, pp. 537–571. doi.org/10.1007/978-1-4614-0046-2_29