

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

### Review

# State of the art and review on the treatment technologies of water reverse osmosis concentrates

### A. Pérez-González, A.M. Urtiaga, R. Ibáñez, I. Ortiz\*

Dpto. Ingeniería Química y QI. ETSIIyT, Universidad de Cantabria, Av. de los Castros s/n, 39005 Santander, Spain

### ARTICLE INFO

Article history: Received 5 July 2011 Received in revised form 19 October 2011 Accepted 20 October 2011 Available online 31 October 2011

#### Keywords:

Reverse osmosis concentrates Volume reduction Pollutant load reduction Salt recovery Nutrient recovery

#### ABSTRACT

The growing demand for fresh water is partially satisfied by desalination plants that increasingly use membrane technologies and among them reverse osmosis to produce purified water. Operating with water recoveries from 35% to 85% RO plants generate huge volumes of concentrates containing all the retained compounds that are commonly discharged to water bodies and constitute a potentially serious threat to marine ecosystems; therefore there is an urgent need for environmentally friendly management options of RO brines.

This paper gives an overview on the potential treatments to overcome the environmental problems associated to the direct discharge of RO concentrates. The treatment options have been classified according to the source of RO concentrates and the maturity of the technologies. For the sake of clarity three different sources of RO concentrates are differentiated i) desalination plants, ii) tertiary processes in WWTP, and iii) mining industries.

Starting with traditional treatments such as evaporation and crystallization other technologies that have emerged in last years to reduce the volume of the concentrate before disposal and with the objective of achieving zero liquid discharge and recovery of valuable compounds from these effluents are also reviewed. Most of these emerging technologies have been developed at laboratory or pilot plant scale (see Table 1). With regard to RO concentrates from WWTP, the manuscript addresses recent studies that are mainly focused on reducing the organic pollutant load through the application of innovative advanced oxidation technologies. Finally, works that report the treatment of RO concentrates from industrial sources are analyzed as well.

© 2011 Elsevier Ltd. All rights reserved.

\* Corresponding author. Tel.: +34 942 20 15 85; fax: +34 942 20 15 91.

E-mail address: ortizi@unican.es (I. Ortiz).

0043-1354/\$ — see front matter 0 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.watres.2011.10.046

Abbreviations: AA, activated alumina; AOP, advanced oxidation process; BAC, biological activated carbon; BDD, boron doped diamond; BOD, biological oxygen demand; BWRO, brackish water reverse osmosis; CDI, capacitive deionization; CESP, chemically-enhanced seeded precipitation; COD, chemical oxygen demand; DOC, dissolved organic carbon; ED, electrodialysis; EDBM, electrodialysis with bipolar membranes; EDR, electrodialysis reversal; EFC, eutectic freeze crystallization; FBAR, fluidized bioactive adsorber reactor; FBC, fluidized bed crystallization; FO, forward osmosis; GAC, granular activated carbon; ICD, intermediate chemical demineralisation; MCr, membrane crystallizer; MDC, membrane distillation coupled with crystallization; PDO, Petroleum Development Oman; PLE, polimeric ligand exchange; RO, reverse osmosis; SCR, solid contact reactor; TAN, total ammoniacal nitrogen; TOC, total organic carbon; UF, ultrafiltration; VMD, vacuum membrane distillation; WAIV, wind aided intensified evaporation; WWTP, wastewater treatment plant; ZLD, zero liquid discharge.

### Contents

1.	Intro	Introduction						
2.	RO c	RO concentrates from desalination plants: treatment alternatives						
	2.1.	2.1. Solar evaporation						
	2.2.	ing technologies	272					
		2.2.1.	Systems aiming to achieving Zero Liquid Discharge	273				
		2.2.2.	Emerging technologies for salts recovery	276				
3.	RO c	oncentra	ates from wastewater treatment plants: treatment alternatives	276				
	3.1.	Advanced oxidation processes (AOPs) applied to RO concentrates from WWTPs						
		3.1.1.	Ozonation	277				
		3.1.2.	Fenton process	277				
		Photocatalysis and photooxidation	278					
		3.1.4.	Sonolysis	278				
		3.1.5.	Electrochemical oxidation	278				
	3.2. Recovery of nutrients and salts from RO concentrates from WWTP's							
4.	. RO concentrates from industrial water sources: treatment alternatives							
5. Conclusions								
	Acknowledgements							
	References							

### 1. Introduction

Reverse osmosis is a membrane technology widely applied in water desalination, production of potable water and more recently in tertiary wastewater treatment. This technology has the advantages of membrane processes such as modular construction and small footprint, which allow the combination with other treatment processes (Chelme-Ayala et al., 2009).

The technology employs semi-permeable membranes that allow to separate a solution into two streams: permeate, containing the purified water that passes through the membrane, and concentrate, the portion that contains salts and retained compounds and therefore needs a suitable and environmentally friendly management option (Mauguin and Corsin, 2005).

The characteristics of the waste stream, named concentrate, retentate or brine, depend on the quality of the feed water, the quality of the produced water (recovery varies from 35% to 85%), the pretreatment method (added chemicals) and cleaning procedures used (Chelme-Ayala et al., 2009; Greenlee et al., 2009; Squire et al., 1997; Watson, 1990). Then constituent concentrations in the retentate are found to be double or higher than that in feed water (Chelme-Ayala et al., 2009).

Brine disposal in coastal desalination plants has been solved by direct discharge to seawater. In desalination plants, generation of brine is about 55% of collected seawater (Meneses et al., 2010). Recent estimates suggest that up to 25 million m<sup>3</sup> of desalinated water is produced daily around the world (Lattemann and Höpner, 2008). Representative examples of large membrane reverse osmosis seawater desalination plants with ocean outfalls for concentrate discharge are the 330,000 m<sup>3</sup>/day plant in Ashkelon, Israel; the 136,000 m<sup>3</sup>/ day Tuas Seawater Desalination Plant in Singapore; the 64,000 m<sup>3</sup>/day Larnaka Desalination Facility in Cyprus, and the majority of the large desalination plants in Spain, Australia and the Middle East (Voutchkov, 2011).

Roberts et al. (2010) have reported an outstanding literature review on the ecological impacts of desalination plants concluding that there is a widespread belief and recognition that brine discharge poses a potentially serious threat to marine ecosystems. Laboratory-based experiments, toxicological investigations and manipulative field experiments clearly demonstrate the potential for brines and their constituents to illicit adverse impacts on aquatic organisms when present at sufficient concentrations. In addition to the destructive saline properties of the concentrate, in the case of thermal desalination, the brine is usually hotter than the local recipient water body, a circumstance that has also been shown to cause further environmental damage, especially to fragile ecosystems such as corals. Furthermore, during pre- and post- treatment processes a variety of chemical agents are added to enhance flocculation, prevent foaming or to avoid membrane deterioration (Meerganz von Medeazza, 2005). Research on the development of effective anti-scalants with no biological effects may assist in the production of less toxic brines in the future (Roberts et al., 2010). But with the traditional option of direct release to seawater, those components are discharged along with the brine as well as certain metals (copper, nickel, iron, chromium, zinc, etc.) coming from thermal corrosion processes. Thus, as a result of brine direct discharge the most pronounced effects on receiving waters are eutrophication, pH value variations, and accumulation of heavy metals as well as sterilizing properties of disinfectants (Meerganz von Medeazza, 2005). Due to these negative effects, direct disposal to seawater of RO concentrates is doomed to disappear.

One mechanism that has been applied to reduce adverse environmental effects of brine relies on its dilution with power plant cooling waters (Einav and Lokiec, 2003). Brines can be also diluted with natural seawater or municipal wastewaters to reduce salinity prior to discharge (Meneses et al., 2010; Roberts et al., 2010) although the effects of disposal of diluted concentrates can also affect to sensitive species so the solution should be appropriate to local conditions (Meneses et al., 2010). To minimise areas of ecological impacts and limit the intrusion of brines into seawater intake areas the optimum infrastructure design and construction has been studied (Altayaran and Madany, 1992). Dispersion models are used to choose the discharge point with less environmental impact (Del Bene et al., 1994) but these structures appear to have limited success and the environmental damage is also incurred. Groundwater desalination has been reported as a more environmentally friendly alternative to seawater desalination because the discharged brines are less salty than those produced from seawater desalination (Muñoz and Fernández-Alba, 2008).

Traditionally, options for disposal of the concentrates from inland desalination plants have been deep well injection and surface water discharge, or concentration of brines in evaporation ponds (Ahmed et al., 2001; Arnal et al., 2005; Chelme-Ayala et al., 2009; Gabelich et al., 2010; Greenlee et al., 2009; Malaeb and Ayoub, 2011; Muniz and Skehan, 1990). Similar options of RO concentrates management have been used in the case of potable water production from brackish groundwater (Malaxos and Morin, 1990; Squire, 2000; Van Der Bruggen et al., 2003). Inland plants have to solve the problem of concentrate disposal without the possibility of their discharge to seawater, so the development of other management options is an urgent demand.

The cost of brine disposal is another important issue that must be taken into account. In coastal desalination plants the cost of brine disposal to the sea ranges from 5 to 33% of the total cost of desalination (Ahmed et al., 2001) being the disposal cost higher for inland desalination plants than for coastal plants where brine is discharged into the sea (Arnal et al., 2005). In both cases, the cost of brine disposal depends on the brine characteristics, level of treatment before disposal, disposal method and brine volume (Arnal et al., 2005; Malaeb and Ayoub, 2011). With regard to inland desalination plants, depending on the salinity of the concentrate, the cost associated to brine disposal could be considerably higher than in coastal plants (Stanford et al., 2010).

Among the wide diversity of RO applications, this review is mostly focused on the conventional and emerging treatments for RO concentrates generated in desalination plants. Furthermore due to the increasing trend of using RO units in the tertiary treatments of WWTPs the most suitable treatment alternatives for this application are also addressed. Table 2 displays the average chemical characteristics of representative RO concentrates from both applications. Conductivity, total dissolved solids and chloride concentration present significantly higher values in RO brines from desalination

Table 1 – Evaluation of viability of treatment technologies applied to RO concentrates.								
RO concentrates source	Technology	Technological maturity	Operation drawbacks and economic considerations					
Desalination plants	Solar evaporation	Industrial application	Large land areas					
	(Evaporation ponds)		Low productivity					
			Moderate investment and maintenance cost					
	WAIV	Pilot plant scale	Industrial feasibility not proved					
	wind aided intensified evaporation		Moderate investment cost					
	Membrane distillation	Laboratory level	Difficult operational control					
			Scaling and fouling					
			Moderate energy consumption					
	Forward osmosis	Laboratory level	Use of drawn solution					
			Moderate energy consumption					
	Liquid—liquid extraction	Laboratory level	Several treatment stages					
			Extractants consumption					
Wastewater treatment	Ozonation	Laboratory level	High chemical dosage					
plants			High investment cost					
	Fenton processes	Laboratory level	High chemical dosage					
			Moderate investment cost					
	Photocatalysis and photooxidation	Laboratory level	High chemical dosage					
			Moderate energy consumption					
	Sonolysis	Laboratory level	High energy consumption					
	Electrochemical oxidation	Laboratory level	High energy consumption					
			Moderate investment cost					
	Adsorption	Laboratory level	Regeneration of exhausted resins					
			(High chemicals consumption)					
Desalination and	Electrodialysis	Pilot plant scale	Maintaining energy efficiency with					
wastewater			high saline concentrates					
treatment plants			Precipitation on the membrane					
			High capital and operation cost					
	Crystallization	Laboratory level	Stricted operational conditions					
	SAL-PROC	Patented process	Applicability to RO concentrates					
			not completely proved					
Other industrial	EFC	Pilot plant scale	Complex control of operation					
sources			Moderate energy consumption					

Table 2 – Characterization of RO concentrates.																			
	RO concentrates from desalination plants RO concentrates from wastewate									er trea	tment p	lants							
	Ji	Mart	inetti	Korngold	Macedonio	Hajbi	Ahmed	Ersever	Zhou	Westerh-	Van	Van	Pérez	Radjenovic	Chaplin	Lee	Lee	Badruz-	Kumar
	et al.,	et	al.,	et al.,	et al.,	et al.,	et al.,	et al.,	et al.,	off	Hege	Hege	et al.,	et al.,	et al.,	et al.,	et al.,	zaman	et al.,
	2010	20	09	2009	2011	2010	2003 <sup>,b</sup>	2007a' <sup>a</sup>	2011 <sup>,a</sup>	et al.,	et al.,	et al.,	2010 <sup>,a</sup>	2011 <sup>,a</sup>	2010	2009a	2009b <sup>,a</sup>	et al.,	2007
										2009	2002	2004 <sup>,a</sup>						2009	
Parameters																			
Turbidity, NTU	_	_	-	-	-	-	-	-	3.2	-	-	-	2	_	-	-	-	-	-
DOC, mg/L	_	_	_	-	-	-	-	-	-	40	-	-	23.3	57.2	19.2	-	-	-	-
COD, mg/L	_	_	_	-	-	-	-	-	60	138	158	184	_	-	_	64.6	-	-	-
TOC, mg/L	2	-	-	-	-	-	-	40	18	-	-	-	-	-	-	18.4	24.5	25	-
TKN, mg/L	-	-	-	-	-	-	-	-	10	-	-	-	-	-	-	-	-	-	-
TAN, mg/L	-	-	-	-	-	-	-	-	-	-	37.5	34	-	-	-	-	-	-	-
NH4, mg/L	-	-	-	-	-	-	-	80	-	-	-	-	121.8	-	-	-	-	-	-
рН	-	7	8	-	4	7.2	6.2	-	6.9	7	8.2	8.3	7.8	7.6	-	7.2	7.5		-
TDS, mg/L	50,200	-	-	-	-	28,000	17,124	3965	1129	5560	-	-	-	-	-	1218	1276	2950	2750
Conductivity, μS/cm	-	-	-	-	13,500	33,000	25,984	-	1705	10,000	3990	4340	3250	4110	4450	1972	1990	3600	-
Alkalinity, mg/L as CaCO3	-	470	142	-	-	-	345	1006	-	1110	-	-	1233	-	289	-	-	520	-
SiO <sub>2</sub> , mg/L	_	116	72	103	56	-	15.6	-	-	-	-	-	-	-	-	-	-	120	120
Cations																			
Na <sup>+</sup> , mg/L	15,500	991	5130	-	2084	5120	4160	-	203	_	-	-	_	_	435	240.9	226.9	580	910
Mg <sup>2+</sup> , mg/L	2020	318	386	468	245	770	370	-	7	_	-	32	_	_	122	7.1	11.5	9.7	5
K <sup>+</sup> , mg/L	_	_	-	-	79	-	134	-	62	_	-	-	_	_	22.6	65.3	38.4	88	24
Ca <sup>2+</sup> , mg/L	625	1032	819	1020	540	2080	1537	-	65	_	-	159	_	-	306	110.1	63.8	96	5
Fe <sup>2+</sup> , mg/L	_	_	_	-	-	-	0.4	-	-	_	-	-	_	0.3	_	-	-	0.1	-
Mn <sup>2+</sup> , mg/L	-	-	-	-	-	-	0.2	-	-	-	-	-	-	230.5	-	-	-	54	-
Anions																			
Cl <sup>-</sup> , mg/L	28,800	2823	8960	6710	4068	14,170	8369	900	256	-	592.9	700	479	1.4	220.1	267.1	333.2	684	2811
SO <sub>4</sub> <sup>2–</sup> , mg/L	3060	1553	1920	2688	2160	5920	2334	1240	217	-	-	-	443	240	1584	218.4	159.1	468	1437
NO <sub>3</sub> , mg/L	-	-	-	-	-	-	14.6	-	91	-	-	-	-	-	3.1	88.5	60.2	296	269
NO <sub>2</sub> , mg/L	-	-	-	-	-	-	-	-	2	-	-	-	-	-	-	8.3	-	-	-
PO4 <sup>3-</sup> , mg/L	-	0.4	2	-	0.04	-	-	20	39	-	-	-	-	_	-	34.7	21.3	10	-
HCO <sub>3</sub> , mg/L	199	576	223	-	-	-	421	-	-	_	-	-	-	-	-	-	-	-	-

a Average value.

b Average composition of reverse osmosis concentrates from desalination plants of Bahja, Rima, Nimr and Marmul of Petroleum Development Oman.

plants than in RO concentrates from wastewater treatment plants. Regarding sulfate, its concentration levels in concentrates from WWTP's are similar to the chloride content while in concentrates from desalination plants, sulphate concentration is 2–8 times lower than the chloride one. Thus, treatment technologies must be adapted to the source of RO concentrates in order to eliminate the problem associated to their composition. For example, concentrates from wastewater treatment plants present higher organic pollutant load but lower salinity than desalination plants RO concentrates, therefore advanced treatments (like advanced oxidation processes (AOPs)) are required to destroy the most persistent pollutants.

Thus, this paper gives an overview on the technologies aimed at reducing the environmental impact of the disposal of RO concentrates according to their origin, the level of development of the technologies and the final objective of the treatment.

### 2. RO concentrates from desalination plants: treatment alternatives

Traditional management of RO concentrates from desalination plants is mainly conditioned by the location of the plant. In coastal desalination plants, RO concentrates are directly discharge to seawater, while in inland plants the traditional option consists on reducing the concentrate volume prior to disposal (Tang and Ng, 2008). Evaporation techniques have been widely applied to concentrate brines, since their application allow to obtain a solid waste easier to be managed than the original waste and a decontaminated liquid flow that can be directly discharged or even reused (Arnal et al., 2005). Due to the adverse effects of brine disposal together with its associated costs, current research is focused on reducing the impact of RO concentrates by reducing the volume and/or by diminishing the pollutant load of these concentrates. Besides, the beneficial use of brine byproducts is also studied and includes the technical feasibility of isolating salts of the required morphology and purity (Stanford et al., 2010). Recovering commercial byproducts from RO concentrates would be the optimum treatment option, as it solves the environmental problem of concentrate disposal, as well as the economic profitability of reverse osmosis is improved at the same time.

#### 2.1. Solar evaporation

Solar evaporation is one of the techniques considered as a common solution for brine disposal (Chelme-Ayala et al., 2009; Greenlee et al., 2009), especially for inland desalination plants in arid and semi-arid areas (Ahmed et al., 2000). The reverse osmosis concentrate is placed in a shallow lined pond which allows the water to evaporate naturally by using the solar energy; after water evaporates the salt is either left in the ponds or removed for disposal (Katzir et al., 2010). Evaporation ponds are relatively easy to construct, require little operation attention compared to mechanical equipment and except for pumps to convey the wastewater to the pond, no mechanical equipment is required (Mickley, 2001). Pond size includes two components: surface area and depth. Pond depths ranging from 25 to 45 cm are considered optimal for maximizing the rate of evaporation (Ahmed et al., 2000).

However, evaporation ponds are scarcely used because they require large land areas, especially if they are located in places with low evaporation rates, whereas they pose a high potential for contamination of groundwater coupled to the risk of leakage underneath the pond (Katzir et al., 2010). Evaporation ponds ranging from 13.6 to 34.3 ha are used for disposal purposes of the concentrate in the desalination plants located in the central region of Saudi Arabia (Ahmed et al., 2000). Besides this extensive land use, evaporation ponds have been criticized because they do not recover the evaporated water (Mickley, 2001). Additionally, the productivity of the process is quite low (around 4 L/m<sup>2</sup>d). This drawback can be overcome by using wet surfaces (capillaries or clothes) exposed to wind action to increase the evaporation surface. Arnal et al. (2005) tested different adsorbent materials in order to improve the water evaporation rate of brines from desalination plants. According to the experimental results, the most suitable adsorbent for natural evaporation was a rectangular cloth made of cellulose (65%) and cotton (35%). It was also concluded that air velocity improved natural evaporation, although the overall efficiency was limited by the blowing of solids onto the surface of water.

Following this investigation line, a proprietary technique WAIV (Wind Aided Intensified eVaporation) was developed as alternative to natural evaporation. WAIV is a less land intensive method to reduce brine volumes by the use of the drying power of the wind without generating small droplets that can cause salt drift. This configuration employs recirculation of brines as falling films on vertical hydrophilic surfaces that are largely mounted parallel to the wind direction (Macedonio et al., 2011). When exposed to the dry winds of semi-arid regimes, these surfaces are cooled to near the wet bulb temperature and the difference of temperature between the warmer wind and the cold-water surface drives heat flux to the wetted surface. The vapour pressure gradient drives the evaporation mass transfer from the surface. Previous studies on normal desalination brines in a pilot unit with 31–43 m<sup>2</sup> wetted evaporation surfaces showed that evaporation rates (L/D-m<sup>2</sup>) can be improved by 50–90% relative to open ponds while surface loading reached 15-30 m<sup>2</sup>/m<sup>2</sup> footprint. For example, the Sabha seawater RO plant located near the Red Sea port of Eilat sends its rejected brine to salt production evaporation ponds. A pond area of 700,000 m<sup>2</sup> is needed in order to handle about 5000 m<sup>3</sup> per day of concentrate. It was estimated (Katzir et al., 2010) that a WAIV installation could reduce the required land area by an order of magnitude. To evaluate the performance of several evaporation surfaces, Gilron et al. (2003) tested a pilot unit using brines from Mekorot's Sabha B desalination installation in Eilat. The total dissolved solids (TDS) content of the brine was around 16,000–18,000 ppm and it was supersaturated with respect to sparingly soluble calcium salts. Better results were obtained when using materials with no internal surfaces (netting) that are less susceptible to plugging than those with internal surfaces (nonwoven geotextiles). The WAIV technology was further studied in order to recover salts that can be potentially useful as raw materials (Katzir et al., 2010). Concentrates obtained in the RO and ED treatment of saline groundwater were

evaporated. Gypsum precipitation on the evaporation surfaces and in the feed basin was observed, leading to an enrichment of magnesium relative to sodium ion in the resulting concentrate brine. This technology can be an interesting option whenever precipitated salts are recovered. Although WAIV presents advantages with respect to evaporation ponds in land use, the availability of this technology has been only demonstrated at laboratory scale.

### 2.2. Emerging technologies

Conventional treatments, like concentration in evaporation ponds, have several disadvantages such as extensive land use and low productivity. Thus, investigation on new options to improve the management of reverse osmosis concentrates is a current demand.

In this section we review the potential of several emerging technologies focused on the treatment of RO concentrates from desalination plants, classified according to the operation objective.

Membrane distillation has been studied as alternative for the processing of highly concentrated aqueous solutions. Vacuum Membrane Distillation (VMD) is an evaporative technology that uses a membrane to support the liquid--vapour interface (Urtiaga et al., 2001). The main advantages of membrane distillation over conventional distillation processes are that the operating temperature is in the range of 60–80 °C and that the membranes provide a high contact area per unit of equipment volume, allowing very compact installations and reduced footprint. Mericq et al. (2010) simulated an increase from 40% to 89% in the water recovery of a 40.000 m<sup>3</sup>/ day RO plant fed with seawater together with a reduction of the brine volume by a factor of 5.5 after coupling RO with VMD. The model used for this simulation was based on experimental results obtained at a bench-scale batch unit. In the experiments developed with real RO brines organic fouling or biofouling was not observed, at least at the time scale of a few hours. However, for high salt concentrations, calcium scaling occurred although its impact on the permeate flux was very limited. Scaling effects of CaCO<sub>3</sub> and CaSO<sub>4</sub> in membrane distillation operated at high seawater concentrations have been deeply studied (Curcio et al., 2010; He et al., 2008), being the main conclusions that scaling reduces the transmembrane permeate flux as membrane promotes heterogeneous nucleation mechanisms. Also, the detrimental effect of the presence of humic acid substances became significant at higher concentration factors. Nevertheless, calcium scaling was found to be reversible after appropriate washing and chemical cleaning. Calcium scaling could also be controlled by accelerated precipitation softening prior to the direct contact membrane distillation of the RO concentrate obtained in a drinking water treatment facility (Qu et al., 2009, 2010).

Membrane distillation coupled with crystallization (MDC) was investigated in a bench-scale plant operated with brines discharged from a seawater reverse RO unit (Ji et al., 2010). The major advantage of the MDC process is its capability to concentrate the salt up to the supersaturated state, which allows its crystallization (Gryta, 2002). In MDC, the high contact area provided by hollow fiber membranes allows to achieve reliable evaporation fluxes at moderate temperatures

(40–50 °C) with energy consumption of about 15–20 kW h/m<sup>3</sup>, while conventional evaporative equipments for NaCl crystallization need to operate at temperatures higher than 70 °C, with specific energy consumption of about 30 kW h/m<sup>3</sup>. However the main problem of membrane distillation is that the technology is not yet commercially available at industrial scale (Singh, 2009).

In a recent study (Ji et al., 2010) seawater was collected from the Tyrrenian Sea in Amantea (Calabria) and further processed in an RO lab-scale unit. Lime/soda ash softening was applied to the RO concentrate to reduce calcium and magnesium hardness and to limit scaling problems. Experiments were focused on NaCl crystallization, obtaining a production of 17 kg/m<sup>3</sup> of NaCl crystals, representing 34% of the total content of dissolved solids in the brine. In conclusion, membrane distillation-crystallisation was reported to be a feasible technique to concentrate RO brines, achieving water recovery efficiency higher than 90%.

Applying electrodialysis (ED) to brine effluents, their salt concentration is increased from 0.2 - 2% to 12-20% with an energy requirement of 1.0-7.0 kW h/m<sup>3</sup> in contrast to approximately 25 kW h/m<sup>3</sup> needed by thermal evaporation (Korngold et al., 2005, 2009). In ED operation, there are two major technical problems to be overcome: firstly to find solutions for operating at concentrations up to 20% of salts without significantly diminishing the energy efficiency and secondly to prevent CaSO<sub>4</sub> precipitation on the membrane. This last drawback can be prevented by continuous removal of gypsum from the brine in a separate precipitator. ED experiments were carried out using the brine obtained from the RO desalination of brackish water as the feed to an ED pilot plant combined with a gypsum precipitation step (Korngold et al., 2005, 2009), as it is depicted in Fig. 1. After 600 h of operation, the amount of CaSO4 that precipitated was approximately 0.15 eq. CaSO<sub>4</sub>/h, and scaling on the membrane was prevented. Besides, significant acceleration of the precipitation can be achieved by seeding the oversaturated solution with 10-25 g CaSO<sub>4</sub>/L. A very low concentration (0.5-1 ppm) of antiscalant (Calgon) diminished the seeding effect on gypsum precipitation and increased the onset of precipitation time.

Forward osmosis (FO) is presented as an innovative technique to reduce brine volume, having as main advantage lower energy requirement than RO. FO utilises a highly concentrated solution generally referred to as the draw



Fig. 1 – Simplified scheme of ED pilot plant combined with a gypsum precipitation step (Korngold et al., 2005).



solution to generate an osmotic pressure differential across the membrane, thus resulting in the transport of water from the less concentrate feed stream to the highly concentrated draw solution. A wide range of draw solutions can be used: sulphur dioxide, aluminium sulfate, fructose, ammonium bicarbonate, etc (Neilly et al., 2009). Tang and Ng (2008) tested three types of membranes using a concentrate feed of 1 M-2 M NaCl, model brine concentrations, and a draw solution of fructose 5 M-6 M, which was kept constant by adding a suitable amount of fructose periodically. It was found that fructose is not an ideal draw solute as it is not efficient in establishing a high effective driving force. However, using as draw solution NaCl (50 g/L) with less saline concentrates (~0.25 M of chloride), recovery rates larger than 90% were achieved (Martinetti et al., 2009). In both cases, this technique has as inconvenient the need of a draw solute to create an effective driving force that allows water flux, and besides the economic feasibility of the technology has not been demonstrated (Singh, 2009).

2.2.1. Systems aiming to achieving Zero Liquid Discharge One of the most innovative investigation line focused on reducing the concentrate volume to the highest point is called Zero Liquid Discharge (ZLD), which is aimed to achieve the maximum water recovery, through several stages of treatment in order to avoid liquid effluent disposal.

Studies related to this objective have been classified according to the treatment scheme as Basic ZLD systems, Type A, Type B and Type C scheme (see Fig. 2). Table 3 summarizes these schemes alongside the global recoveries achieved with the application of these treatment combinations.

The basic combination is a RO tandem (Primary RO + Secondary RO). Al-Wazzan et al. (2003) increased the product water recovery using brine staging, and besides a reduction of 37% in specific power consumption in a pilot scale unit was achieved. This brine staging unit was in operation during almost 5 months, being their availability of 97%. The use of tandem RO was also studied by several authors (Ning and Troyer, 2009; Ning et al., 2010; Singh, 2009), who asserted that there is a need of intermediate treatment in tandem processes to increase the recovery and avoid precipitation. These systems achieve high recoveries, although the zero discharge goal is not accomplished.

Fouling and precipitation of scaling compounds are two of the main limiting factors for the RO recovery, as mentioned above. Antifouling and anti-scalants compounds are usually added to feedwaters in order to avoid the diminishing of

Table 3 – Treatment processes aimed at Zero Liquid Discharge.									
		Tr	Overall recovery	References					
Basic ZLD scheme	Primary RO		Secondary RO		88–99%	Al-Wazzan et al., 2003; Ning and Troyer, 2009; Ning et al., 2010; Singh, 2009			
Type A ZLD scheme	Primary RO	Ion exchange Resins for silica removal	Secondary RO			Acevedo et al., 2010			
	Primary RO	Precipitation treatment (alkaline-induced)	Secondary RO		87—97%	Gabelich et al., 2007, 2011; Ning et al., 2006; Rahardianto et al., 2010			
Type B ZLD scheme	RO Primary RO	WAIV Secondary RO	Membrane crystallizer Precipitation treatment (calcium sulfate, magnesium, iron and silica)		77–89%	Macedonio et al., 2011 Ning and Tarquin, 2010			
	RO Primary RO	Secondary RO	ED/EDR EDR + UF	WAIV	92% >98%	Turek et al., 2009 Oren et al., 2010			
Type C ZLD scheme	Primary RO	Lime-soda treatment	Secondary RO	Evaporation	80—90%	Mohammadesmaeili et al., 2010a, b			
	Primary RO	Intermediate treatment (several options)	Secondary RO	Brine concentrator + Pond	~100%	Bond and Veerapaneni, 2008			

Fig. 3 – Bipolar membrane electrodialysis scheme for obtaining mixed acid and basis.

membrane performance. However, the addition of these compounds can have negative effects in the post-treatment of RO concentrates. Greenlee et al. (2011, 2010a, 2010b) studied the effects of anti-scalants in the precipitation of scaling salts, like calcium carbonate, as intermediate stage in a tandem RO system. It was demonstrated that anti-scalants decreased the precipitate particle size and change the shape of the particles. Following the objective of increasing the global recovery of RO operation, several authors (Acevedo et al., 2010; Gabelich et al., 2007, 2011; Ning et al., 2006; Rahardianto et al., 2010) proposed RO tandem processes combined with an intermediate unit in order to eliminate the most problematic substances such as foulants and scalants (Type A scheme in Fig. 2). Acevedo et al. (2010) evaluated the possibility for silica concentration reduction by using ion exchange columns with strong basic anionic resins, and reported that the removal of silica strongly

depends on the pH being available at pH over 8.5, when it also takes place calcium and magnesium precipitation. Therefore, Acevedo proposed as another phase of the research a train of cationic and anionic resins to first remove hardness and allow to increase the pH without precipitation. Studies about salts and silica removal were also developed by Gabelich et al. (2007, 2011) who proposed intermediate chemical demineralization (ICD) that consisted on a solid contact reactor (SCR) followed by a filtration stage. Ning et al. (2006) used a limesoftening unit to reduce the limiting foulants of silica and barium sulphate. With the same objective of eliminating antiscalants and fouling compounds, Rahardianto et al. (2010) proposed a two step chemically-enhanced seeded precipitation (CESP) for accelerated desupersaturation. They reported that the resulting lab and pilot plant data would serve as possible scale-up information although control and operation strategy had to be developed to maintain consistently high demineralization efficiency at industrial level.

Other schemes have been investigated with the aim of recovering both salts and water (Neilly et al., 2009). These systems are characterized for having one or more final steps of post-treatment of the concentrate obtained from the second RO stage (Type B scheme in Fig. 2) (Macedonio et al., 2011; Ning and Tarquin, 2010; Oren et al., 2010; Turek et al., 2009; Zhang et al., 2010). Combining WAIV technology with a membrane crystallizer (MCr), Macedonio et al., 2011 achieved recovery factors as high as 88.9% and capital cost of WAIV was reduced in a 64% in comparison to conventional ponds. Ning and Tarquin (2010) studied the fractional crystallization of salts before thermal evaporation of water. In turn, Turek et al. (2009) studied the combination of RO with electrodialysis reversal (EDR) achieving 91.6% of water recovery, although the synthetic water used had no comparable composition with real RO concentrates. Oren et al. (2010) proposed a system based on further concentration of the BWRO brine with EDR and WAIV. Scaling of ED unit was prevented by acidification, operating the electrodialysis in a reversal mode, and a side loop crystallizer which prevented build-up of scaling components. The super-concentrate from the EDR unit was further concentrate in a wind powered WAIV unit that brought final TDS to more of 30%, and showed



Fig. 4 – Experimental set-up for treatment of RO brine using ozone + BAC column + CDI (Lee et al., 2009a, b).





Fig. 5 - Salt recovery scheme used by Mohammadesmaeili et al. (2010a, b).

promise as a method to recover mineral byproducts. Cost effectiveness of these process alternatives need to be assessed in order to determine their availability and profitability.

The third type of ZLD scheme is based on combining type A and type B ZLD scheme. Mohammadesmaeili et al. (2010a, b) proposed a system with and intermediate stage of lime softening and several stages of evaporation—crystallization after the secondary RO (see Fig. 5). Results of this research are explained in more detail in Section 3.2. This type of scheme was also studied by Bond and Veerapaneni (2008); they affirmed that treatment costs and energy requirements of ZLD can be reduced by adding the intermediate steps of concentrate treatment and secondary RO. They evaluated different options of intermediate treatment: chemical precipitation with sodium hydroxide (NaOH) or lime  $[Ca(OH)_2]$ , fluidized bed crystallization (FBC), adsorption on activated alumina (AA), chemical precipitation with alum  $[Al_2(SO_4) \cdot 14H_2O]$  and ion exchange. FBC has been demonstrated to produce a much smaller volume of solids than that produced by conventional softening. Besides, the evaluation of treatment costs comparing the system without intermediate treatment (benchmark process) with the system with FBC and microfiltration (ZLD process) shows that treatment cost would be reduced by 50–70%, and energy consumption would be reduced by 60–75%. An important number of brine concentrators are in operation in United States. Operating



Fig. 6 - Electrochlorination system proposed by Badruzzaman et al., 2009.

experiences of plants using brine concentrators to concentrate reject streams have shown that this is a viable application and the system is highly reliable (Mickley, 2006).

Treatment schemes based on ZLD objective are pointed to be a promising option for the treatment of RO concentrates. Initial estimation about treatment costs indicates that these systems would be feasible, but it would be necessary leap from pilot plant to industrial level to safely evaluate the applicability of these systems.

### 2.2.2. Emerging technologies for salts recovery

Recovering commercial products is the final challenge to improve the management of RO concentrates whatever their water source is. If valuable substances are recovered from RO concentrates a double objective will be achieved: the reduction of the environmental impact of RO concentrates disposal added to the improvement of the economy of the global treatment process.

Through combination of evaporation and crystallization technologies, valuable salts can be recovered. Hajbi et al. (2010) analysed the solubility diagrams of the hexary system Na<sup>+</sup>, K<sup>+</sup>,  $Mg^{2+}$ ,  $Ca^{2+}/Cl^{-}$ ,  $SO_4^{2-}//H_2O$  to define crystallization paths that they used for the experimental design. Their results assessed the potential of recovering salts like NaCl, KCl, CaSO<sub>4</sub>·2H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O, ... through the isothermal and isobaric evaporation of the rejected brine. Several studies on the viability of producing salts from RO concentrates of desalination plants managed by Petroleum Development Oman (PDO) were developed by Ahmed et al. (2003). The viability study was focused on the application of the patented SAL-PROC process consisting on the sequential extraction of dissolved elements from inorganic saline waters in the form of valuable chemical products in crystalline, slurry and liquid forms. The potential products that can be recovered would be gypsum-magnesium hydroxide (mixture), magnesium hydroxide, sodium chloride, calcium carbonate, sodium sulfate and calcium chloride. In light of the estimations, processing the  $405 \times 10^6$  L/year of the rejected brine generated in the four PDO desalination plants would make possible to produce commercial salts worth US \$895,000 in the most optimistic scenario. Although the economic profit is not so high, it is indisputable that the recovery of potential commercial salts is a great option to improve the cost-effectiveness of desalination processes. Regarding the market of inorganic salts, a quantitative assessment of the global market of recovered salts is not available yet because technologies are in an early development stage, but it has been reported that market could hold the produced salts. According to Ahmad and Williams in the United States 45 million tons of salts are produced annually and about 70% of these salts are used by chemical industries (Ahmad and Williams, 2011.). On the other hand Van Houwelingen stated that in the Netherlands the market of recovered salts would not be a problem since all solids generated in fluidized bed crystallization (FBC) processes for the treatment of reverse osmosis concentrates are put to beneficial use by other industries, such as steel production (Bond and Veerapaneni, 2008).

Production of mixed acids and mixed bases using Electrodialysis with Bipolar Membranes EDBM (see Fig. 3) is another viable option. Mavrov et al., 1999 obtained suitable acids and bases mixtures for the regeneration of ion exchangers by processing RO concentrates from desalination of surface water. EDBM has been also applied to RO concentrates from wastewater treatment plants, so this technology will be widely explained in the Section 3.2.

Jegatheesan et al. (2009) evaluated the recovery of valuable metals from concentrates by means of liquid-liquid extraction. The recovery ratio for rubidium using BAMBP [4-tertbutyl-2-(a-methylbenzyl) phenol] or 4-sec-butyl-2-(a-methylbenzyl) phenol] as extractants was higher than 80% (Jeppesen et al., 2009). Liquid-liquid extraction has been also applied by Le Dirach et al. (2005) to recover materials from the concentrated brine of the RO plant in Skhira (Tunisia). The treatment process is divided in several extraction stages: phosphates extraction using a blend of iron and aluminium sulphates, liquid-liquid extraction to recover cesium, liquid-liquid extraction to recover indium and gallium, rubidium extraction, evaporation of the remaining brine to recover carnallite crystals  $KMgCl_3 \cdot 6H_2O$  and as final step, extraction of germanium and magnesium. Still, these separation protocols have been studied at viability scale and require final demonstration.

## 3. RO concentrates from wastewater treatment plants: treatment alternatives

In recent years, reverse osmosis has been also applied to further treat the secondary effluents of wastewater treatment plants. These RO concentrates present less salinity than RO concentrates from desalination plants although larger amounts of organic matter, including persistent micropollutants, are contained. Solley et al. (2010) reported that the contaminants in these streams could be 6–7 times more concentrated than in the feed water. Therefore specific treatments, such as advanced oxidation processes (AOPs), have been researched in order to reduce the pollutant load.

Most of the reported studies are focused on the reduction of a global parameter that resembles the organic contamination such as the chemical oxygen demand (COD) and the Total Organic Carbon (TOC), although the removal of other pollutants has been also explored. For example, Ersever et al. (2007a, b) studied the removal of nitrogen compounds from RO brines through biological nitrification-denitrification and sulfate reduction via a fluidized bioactive absorber reactor (FBAR) process and using granular activated carbon (GAC). Experiments were conducted at different hydraulic retention times and nitrate concentrations, showing that the FBAR process could be an efficient technology for nitrogen removal of RO concentrates, although nitrogen was considered a minor pollutant, recent characterisation of RO concentrates from WWTPs shows concentrations of ammonia up to 120 mg/L (see Table 2), turning the interest to the referred technologies.

Traditional treatments such as coagulation and activated carbon adsorption were tested for DOC (dissolved organic carbon) removal in RO concentrates (Dialynas et al., 2008). Experimental results showed that ferric chloride is a better coagulant than aluminium sulfate ( $Al_2(SO_4)_3 \cdot 18H_2O$ ), achieving 52% removal of DOC. Ferric coagulation tests effectively removed colour (79%) while DOC and COD mostly due to low molecular weight compounds were removed up to 34% and 49% respectively (Bagastyo et al., 2011b). However, other authors (Zhou et al., 2011) reported lower efficiencies of coagulation, attributed to the different characteristics of the wastewater investigated.

Adsorption on activated carbon (AC) was studied at different carbon doses. The highest removal observed was 91% for the dose of 5 g/L, so results of DOC removal with GAC adsorption are more promising than in coagulation tests. Similar results have been reported by Zhou et al. (2011), and as in previous works, the organics remaining in the RO concentrate were hardly adsorbed at higher AC dosage, indicating the existence of non-adsorbable organic matter fraction.

### 3.1. Advanced oxidation processes (AOPs) applied to RO concentrates from WWTPs

Table 4 summarizes the research on the application of AOPs to RO concentrates. The studies include the well known ozonation and Fenton technologies, the latest developments in photocatalysis and photooxidation, together with new applications of sonolysis and electrooxidation.

### 3.1.1. Ozonation

Feasibility tests of advanced oxidation processes for the removal of organics from the RO concentrate obtained in a water reclamation plant located in Singapore were performed by Zhou et al. (2011). Simple ozone treatment could only remove a small fraction (22%) of DOC with marginal improvements at higher energy input. Nevertheless, O<sub>3</sub> treatment provided better performances that UV irradiation or hydrogen peroxide addition. Meanwhile, it was observed that the combination of ozonation with photocatalysis (UVA/ TiO<sub>2</sub>) enhanced DOC removal up to 52%, while the highest overall efficiency was obtained by the combined UVA/TiO<sub>2</sub>/O<sub>3</sub> with coagulation pretreatment. Moreover, it was found that the latter combination increased the biodegradability index (BDI =  $BOD_5/COD$ ) of the raw RO concentrate by 7–20 times. The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment applied by Westerhoff et al. (2009) achieved a 75% removal of DOC contained in RO concentrate from the Scottsdale Water Campus facility, although very high

ozone (1000 mg/L  $\rm O_3)$  and hydrogen peroxide (0.7 mol  $\rm H_2O_2/$  mol  $\rm O_3)$  dosages were required.

Ozone pretreatment for a biological activated carbon unit increased the biodegradability of the RO brine obtained from a domestic wastewater treatment facility (Lee et al., 2009a). Laboratory scale batch experiments showed that ozonation alone achieved a maximum TOC removal rate of 24%, while Biological Activated Carbon (BAC) alone provided a limited 23% of TOC removal. However, the synergistic effect of combining ozone and BAC showed a good potential in reducing fouling problems for a subsequent capacitive deionization (CDI) stage (Lee et al., 2009a, b) (see Fig. 4), a method for removing salts contained in aqueous solutions by electroadsortion (Oren, 2008). A capacitive deionization cell unit consists of two electrodes made of activated carbon and separated by the circulating ion containing solution. Electrons are not transmuted by red-ox reactions but by electrostatic adsorption (Strathmann, 2010). On the basis of the results it was claimed that CDI might be an attractive option for desalting water due to its lower energy demand compared to RO.

RO concentrates from wastewater treatment plants contain, among many other pharmaceuticals, beta blockers, that are classified as potentially toxic to aquatic organisms. Because of beta blockers molecules have moieties (amine groups, activated aromatic rings), which are reactive towards ozone, it was tested whether ozonation can be applied for their mitigation. Moderate ozone doses (5–10 mg/L) were found to be sufficient to remove beta blockers efficiently (Benner et al., 2008).

### 3.1.2. Fenton process

Fenton process for the treatment of RO concentrates has not been widely studied Westerhoff et al. (2009) developed Fenton (Fe<sup>2+/</sup>H<sub>2</sub>O<sub>2</sub>) and Fenton-like (Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>) experiments in a jartest apparatus. The Fenton process (pH~3.3; 10 mM Fe<sup>2+</sup> and 10 mM H<sub>2</sub>O<sub>2</sub>) removed up to 50% of DOC; residual iron was precipitated by raising the pH back to 7.5–8.0. Higher DOC removals might have been achieved using higher chemical dosages. No more studies regarding application of Fenton process to RO concentrates have been found in literature.

Table 4 – Advanced oxidation processes (AOPs) applied to RO concentrates.									
AOP applied		Objective	Reference						
Photocatalysis	$TiO_2 + h\upsilon \!\rightarrow\! e^- + h^+$	DOC removal	Dialynas et al., 2008						
	$h^+ + H_2O \rightarrow HO' + H^+$	DOC removal with coagulation pretreatment (FeCl <sub>3</sub> )	Zhou et al., 2011						
		DOC removal 95%	Westerhoff et al., 2009						
Photooxidation	$H_2O_2 + hv \rightarrow 2HO'$	DOC removal	Bagastyo et al., 2011a, b						
		DOC removal	Westerhoff et al., 2009						
Sonolysis	$H_2O+))) \rightarrow H' + HO'$	DOC removal (low)	Dialynas et al., 2008						
	$2HO' \rightarrow H_2O_2$	DOC removal	Zhou et al., 2011						
Electrooxidation	$H_2O + Anode \rightarrow Anode[HO']_{ads} + H^+ + e^-$	COD and TAN removal	Van Hege et al., 2002						
		COD and TAN removal	Van Hege et al., 2004						
		COD, ammonium and emerging pollutants	Pérez et al., 2010						
		N-nitrosodimethylamine destruction	Chaplin et al., 2010						
		DOC and pharmaceuticals and pesticides oxidation	Radjenovic et al., 2011						
Ozonation	$O_3 \rightarrow (H_2O_2, UV) HO'$	DOC removal	Westerhoff et al., 2009						
	()	Beta blockers molecules removal	Benner et al., 2008						
		Improving biodegradability of RO brine	Lee et al., 2009a, b						
Fenton8	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO'$	DOC removal	Westerhoff et al., 2009						

#### 3.1.3. Photocatalysis and photooxidation

From the various advanced oxidation processes, heterogeneous photocatalysis with TiO<sub>2</sub> as catalyst brings the advantage of the possible use of solar radiation. Several recent works deal with the application of UV/TiO<sub>2</sub> to the removal of organic load from RO concentrates. For a RO concentrate with an initial DOC concentration of 10.2 mg/L, dark adsorption and UVA light experiments were performed (Dialynas et al., 2008) using two different catalyst doses (0.5 and 1 g/L TiO<sub>2</sub>). In dark adsorption tests, 30% DOC removal was achieved within 50-60 min at both catalyst concentrations. When UVA light is used during 1 h, the DOC oxidation yield was between 49 and 41% at the high and low catalyst level respectively. The combination of photocatalytic oxidation with coagulation as pretreatment, has been also studied (Zhou et al., 2011). For a raw RO concentrate obtained from a water reclamation plant in Singapore the removal of DOC and COD became rather slow after 1 h of reaction time when using both UVC/TiO<sub>2</sub> and UVA/ TiO<sub>2</sub> treatment processes. This behaviour was assigned to the nature of the remaining organics that were very recalcitrant to both treatment processes. However, the coagulation pretreatment using ferric chloride (FeCl<sub>3</sub>), provided the conditions for the gradual removal of DOC and COD by photocatalysis. After a reaction time of 6 h, 95% and 72% of DOC could be removed by UVC/TiO2 and UVA/TiO2. Similarly, Westerhoff et al. (2009) achieved 95% DOC removal at a UV dose of 10.4 kW h/m<sup>3</sup>, being the removal rate nearly independent of the titanium dioxide dose that was varied between 1 and 5 g/L. When the system UV/H<sub>2</sub>O<sub>2</sub> was used, 40% DOC removal with a UV dose of 11.8 kW h/m<sup>3</sup> and H<sub>2</sub>O<sub>2</sub> dose of 10 mM was achieved. Photooxidation (UV/H<sub>2</sub>O<sub>2</sub>), has been also tested in RO concentrates from a water treatment plant by Bagastyo et al. (2011a). Complete decolourisation and 50-55% of COD removal was achieved.

### 3.1.4. Sonolysis

Organic contaminants can also be degraded by the ultrasonic technique (US) in the presence of a catalyst, acids and nonoxidant gases. The chemical effects of ultrasounds are due to the high temperatures and pressures produced during violent collapse of cavitation bubbles. In water, implosion and fragmentation of the bubble is the centre of energy phenomena: temperature, pressure and electric discharges give rise to  $H_2O$  sonolysis with production of radical species (OH•, H•, HOO•) and direct destruction of solutes (Hoffmann et al., 1996; Farooq et al., 2008).

Results of DOC removal obtained with sonolysis show that this process is less efficient than other AOPs. Testing a RO concentrate with an initial DOC of 10.1 mg/L, only a 29% of the DOC was oxidized in 1 h at 67.5 W. If the energy level is duplicated (135 W) during 1 h of treatment, DOC removal is only increased to 34% (Dialynas et al., 2008). Due to the low DOC removal, the possibility of using sonolysis combined with other AOPs has been studied (Zhou et al., 2011). Using a RO concentrate from a wastewater treatment plant with an initial DOC of 18 mg/L, at 1 h of reaction time, the sequence of DOC removal efficiencies achieved was US < US/H<sub>2</sub>O<sub>2</sub> < US/O<sub>3</sub> < US/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> achieving  $\sim$  31% DOC removal as the highest removal with the last combination.

#### 3.1.5. Electrochemical oxidation

Electrochemical oxidation is a very efficient alternative for the treatment of wastewater containing non-biodegradable organics and ammonium compounds. With regard to RO brine, electrochemical treatment seems a promising technology, as the high salinity of the RO concentrate ensures an excellent electric conductivity that could reduce the energy consumption. Moreover, the high chloride content could facilitate indirect bulk oxidation through the electrogenerated strong oxidants such as hypochlorite and oxidation of total ammonia nitrogen (TAN) and organics can be accomplished simultaneously (Van Hege et al., 2002; Pérez et al., 2010).

Reverse osmosis concentrates from a pilot installation processing a mixed domestic and textile wastewater effluent were tested to determine the characteristics and efficiency of several anode materials (Van Hege et al., 2002, 2004). Comparing RuO<sub>2</sub> and Boron Doped Diamond (BDD) anodes, results showed that current efficiency for BDD anode (35.2%) is more favourable than the efficiency obtained for a RuO<sub>2</sub> anode (14.5%). The higher efficiency of BDD anodes can be attributed to the superior chlorine production rate of this material because of the high selectivity towards the chlorine evolution reaction. Longer treatment times showed the capacity of BDD anodes to provide total removal of ammonium and DOC contained in the RO concentrate generated in a reverse osmosis facility aimed at the industrial reuse of the reclaimed water (Pérez et al., 2010).

Thanks to the good results obtained in COD and ammonia removal, electrochemical oxidation of RO retentates with BDD anodes was also studied for the removal of emerging micropollutants (Pérez et al., 2010) Membrane concentrates contain an increasing amount of salts, organics and biological constituents. Among those organic compounds appear the socalled "emerging pollutants" which include pharmaceuticals, personal care products and other metabolites. These compounds appear in RO concentrates because they are highly rejected by the reverse osmosis membranes, and their removal must be investigated because of the environmental risk associated to their emission to the receiving natural water bodies. RO concentrates from a UF/RO pilot plant that treats the secondary effluent of a WWTP were oxidised electrochemically using BDD anodes (Pérez et al., 2010). Ten emerging pollutants that were found as most prevalent in the secondary effluent of a WWTP were investigated achieving removal percentages higher than 92% after 2 h of electrooxidation. Ibuprofen appears like the most resistant compound to electrochemical treatment, thus needing longer times for complete removal. The influence of the applied current density and the initial concentration of the micropollutants, obtained after different recovery ratios of the RO operation, allowed to conclude that the controlling step of the process kinetics is the mass transfer from the liquid bulk to the surface of the BDD anode due to the low concentration of the target compounds. Moreover, the formation of organochloride compounds was kept at low levels. However, testing RuO<sub>2</sub>/IrO<sub>2</sub>-coated Ti electrodes for elimination of pharmaceuticals and pesticides, Radjenovic et al. (2011) concluded that this type of electrodes should not be used, because chlorine mediated indirect oxidation was the main

mechanism and the organic compounds were transformed into their halogenated derivatives, which are persistent and require extreme treatment conditions. Advantages of BDD anodes were also probed for the elimination of N-nitrosodimethylamine, a highly toxic disinfectant compound present in chlorinated wastewater effluents, and further concentrated in RO retentates (Chaplin et al., 2010). Research focused on the electrooxidation of this compound using BDD electrodes showed its advantage over other AOPs, as oxidation was carried out in the presence of high  $HCO_3^-$  concentrations. This is an advantage over other advanced oxidation processes due to the fact that scavenging effect of  $HCO_3^-$  over hydroxyl radical is not a big drawback in electrooxidation.

### 3.2. Recovery of nutrients and salts from RO concentrates from WWTP's

Evaporation and crystallization steps have been evaluated by Mohammadesmaeili et al. (2010a, b) to recover salts from RO concentrates. To maximize the salts recovery the authors proposed a combined system based on a RO tandem with an intermediate stage of lime softening, and several stages of evaporation-crystallization after the secondary RO system (see Fig. 5). Thanks to the lime-soda treatment, magnesium hydroxide with a purity of 51-58% was obtained. This precipitate also contained 19.5–23.3% of CaCO<sub>3</sub> and 1.3–7.8% of CaSO<sub>4</sub> as impurities. Besides, calcite (CaCO<sub>3</sub>) with a purity of 95% and calcium sulfate with a purity of 92% were obtained as byproducts (Mohammadesmaeili et al., 2010a). After this softening treatment, the brine was treated in a second reverse osmosis unit. Then, an evaporation and crystallization step was carried out and a mixture of Na<sub>2</sub>SO<sub>4</sub> (86-88%) and NaCl (5-14%) was obtained. The final step of the treatment train is an evaporation to dryness of the left effluent and as a result, a mixture of Na $^+$ , SO $_4^{2-}$ , Cl $^-$  and K $^+$  (35–40%, 17–33%, 25–41%, 1-5% respectively was obtained) (Mohammadesmaeili et al., 2010b). The combination of reverse osmosis with evaporation and crystallization has been applied at the Doswell Combined Cycle Power Plant in Hanover County (Virginia) (Seigworth et al., 1995) with the goal of achieving zero liquid discharge. However, in this case the filter cake from the press must be disposed off. Thus, salts recovery by combining evaporation and crystallization is highlighted as a feasible option, although further work is still needed to evaluate the economic aspects of salt production.

Zhang et al. (2009) analysed the viability of recovering valuable compounds from RO concentrates by applying ED. They used ion exchange membranes for the separation of nutrient ions and organic compounds from salts contained in the RO concentrates coming from the treatment of wastewaters of a food company. RO concentrates contained 120 mg/L of phosphate and 120 mg/L of organic compounds measured as TOC. The experimental tests were carried out with synthetic solutions resembling the composition of this RO concentrate (0.45 g/L NaCl, 0.54 g/L MgSO<sub>4</sub>, 0.026 g/L NaNO<sub>3</sub>, 0.69 NaHCO<sub>3</sub>, 0.062 g/L Na<sub>2</sub>HPO<sub>4</sub> and 0–120 g/L TOC). ED tests were carried out to evaluate the performance of two membranes: a non-selective ED membrane (SA) and an ED membrane selective for monovalent anions (MVA). Experimental results reflected that using the MVA membrane,

monovalent anions can be separated from multivalent ions, that later are retained in the diluate compartment. The separation factor was improved by increasing the pH or reducing the applied current. With regard to the organic compounds it was concluded that larger ions are retained more efficiently than the smaller ones, which points to a sizeexclusion mechanism, while zwitterions are retained almost completely in the diluate side. In the same study it was affirmed that in a test carried out with real RO concentrates, more than 85% of the organic fraction remained in the feed while salt concentrations (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) decreased, suggesting that the separation of salts from organics by electrodialysis is feasible. Later studies (Zhang et al., 2010) endorsed that high overall recovery using ED is achieved and a moderate selectivity was observed between  $SO_4^2/Cl^-$  and  $HCO_3^-/Cl^-$  and a moderate to high selectivity was found between Ca<sup>2+</sup>/Na<sup>+</sup> by using the non-selective anion and cation exchange membranes.

Production of mixed acids and mixed basis using Electrodialysis with Bipolar Membranes (EDBM) (see Fig. 3) is also a viable option. For conversion of RO concentrates from wastewater treatment plants into mixed acid and mixed base streams, Badruzzaman et al. (2009) evaluated the use of bipolar membrane electrodialysis (EDBM). Moreover, they proposed electrochlorination (see Fig. 6) for onsite chlorine generation. RO concentrates contain a significant amount of divalent metals, so a Na<sup>+</sup> based cation exchange resin was used to remove them in order to avoid potential precipitation and scaling on the membrane surface. Acid and base production tests were conducted in a batch configuration. The salt concentration in the feed in terms of conductivity went down from 9 mS cm<sup>-1</sup> to less than 2 mS cm<sup>-1</sup>, while the acid and base concentrations of the products was around 0.2 N.

Regarding the separation of nutrients from RO concentrates, adsorption using polymeric resins has been investigated to recover phosphate. The technology seems feasible although phosphate concentrations are not very high, Kumar et al. (2007) analysed the separation of phosphates using polymeric ligand exchange (PLEs) resins and their recovery as struvite. RO concentrates were collected from two pilot integrated membrane systems at the wastewater treatment plant in Rio Rancho (New Mexico) and the North City water reclamation plant in San Diego. The RO concentrate with a low chloride concentration (0.684 g/L Cl<sup>-</sup>) and containing 10 mg/L of phosphate was passed through a packed column loaded with a PLE resin. The regeneration of the exhausted column was conducted using NaCl. In the regenerant solution, P was recovered at a concentration of 78 mg/L. To achieve struvite precipitation, tests were conducted with deionized water spiked with 20 mg P/L to determine the best molar ratio  $(P:Mg^{2+}:NH_4^+:1:1.5:1)$  and then with the recovered solution. Phosphate can be potentially recovered as struvite, although nitrate and sulfate also precipitate.

### 4. RO concentrates from industrial water sources: treatment alternatives

Hypersaline brine production is one of the most important environmental issues in mining industry. RO concentrates have a conductivity similar to RO concentrates from desalination plants (22,000  $\mu S~cm^{-1}$ ) and regarding anion composition, sulfate concentration is much higher than chloride (16,000 mg/L SO\_4^-; 955 mg/L Cl<sup>-</sup>) (Randall et al., 2011). According to this composition, crystallization techniques based on eutectic freeze diagrams were investigated.

Eutectic freeze crystallization (EFC) is based on achieving the eutectic temperature as means to separate aqueous solutions into pure water and solid salts. Because the heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol), the energy required to separate the water as ice is significantly lower than that required to separate it by evaporation. In addition, the simultaneous production of pure ice and pure salt(s) is a major advantage.

The economic advantage of EFC has been analyzed by Nathoo et al. (2009). The authors compared EFC in a tandem crystallizer (see Fig. 7) with an Evaporative Crystallization (EC) system to obtain NaCl·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O. Tests were carried out using reverse osmosis retentates from typical mine water brines containing high levels of sodium, sulfate and chlorine. The temperature in each crystallizer was selected according to the concentrates composition in order to obtain the maximum salt recovery. Taking into account the electricity cost and the salts production, a comparison between EFC and EC concluded that cost saving of using EFC is in the range of 80–85% for the brines under study. In addition, the revenue generated by the sale of the pure salts produced by EFC and the cost of disposal of the mixed salt waste produced by EC were not included in the cost evaluation developed in that study.

The EFC technique has been also evaluated for the treatment of multicomponent hypersaline brine form the eMalahleni (South Africa) Water Reclamation Plant (EWRP), built to address the damage done to the environment and water systems through Acid Mine Drainage. It was concluded that the EFC process could increase the production of the water reclamation plant by 120 m<sup>3</sup>/d while a production of 476 kg/ d CaSO<sub>4</sub>·2H<sub>2</sub>O and 471 kg/d Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O would also be obtained (Randall et al., 2011).

The recovery of pure salts is difficult because they usually have several hydrate forms. Sodium sulfate exists in three hydrate forms: anhydrous  $Na_2SO_4$  (thenardite),  $Na_2SO_4 \cdot 7H_2O$ and  $Na_2SO_4 \cdot 10H_2O$  (mirabilite). Reddy et al. (2010) study the recovery and purity of sodium sulfate using synthetic



Fig. 7 – Simplified EFC process flow sheet (Nathoo et al., 2009).

solutions with a composition simulating brine from the mining industry. Pure water crystals were obtained (<20 ppm impurities) from a synthetic retentate stream. The presence of higher concentrations of NaCl lowers the solubility of Na<sub>2</sub>SO<sub>4</sub> by the common ion effect. A recovery of >90% pure Na<sub>2</sub>SO<sub>4</sub> crystals was obtained from a concentrated NaCl stream prior to any sodium chloride crystals being produced.

### 5. Conclusions

Since direct disposal of RO concentrates from desalination plants is recognised as a practice with adverse impacts on marine ecosystems, the search for environmentally friendly management options is a technological challenge. Thus, in this review, treatment technologies of water reverse osmosis concentrates have been addressed, classified according to the source of RO concentrates and the level of development of each management technology. As the composition of the concentrate is closely related to its source, and the selection of the most suitable treatment is based on the concentrate composition, three different sources of RO concentrates have been reviewed i) desalination plants, ii) tertiary processes in WWTP and, iii) mining industries.

With regard to RO concentrates from desalination plants traditional technologies, such as solar evaporation easy to operate but with a large requirement of land area, give way to more efficient emerging technologies that allow for considerable brine volume reductions such as electrodialysis, forward osmosis, membrane distillation or even its coupling with crystallisation, MDC, that facilitates easy recovery of high purity NaCl crystals. Recovery of salts, nutrients and valuable compounds from RO concentrates is a promising investigation line and thus related works have been collected. However, although thermal brine concentration technologies are well established, they are energy intensive and not cost effective for large-scale applications. In case of freezing processes the initial investment and complexity of operation limit their use.

With regard to the treatment of RO concentrates from WWTPs studies are mainly focused on the reduction of pollutant load and removal of micro-pollutants that could accumulate and cause a high environmental impact. Good results have been obtained applying advanced oxidation technologies and among them electrochemical oxidation with BDD anodes for the removal of micro-pollutants and persistent compounds. Advanced oxidation processes are probably the most promising technologies to degrade and detoxify endocrine disrupting compounds, but the high cost of these technologies may limit their application.

Alternatives aiming at zero liquid discharge, through the combination of individual technologies, are highlighted as the most promising management option in this investigated field. Although studies addressed to this objective are mostly related to RO concentrates from desalination plants, ZLD systems can be applied to any RO concentrate, regardless its origin source. The final objective of ZLD systems must be the recovery of valuable compounds from RO concentrates. Joining both objectives: ZLD and valuable compounds recovery, the problem of RO concentrates management would be solved. However, the main drawback of ZLD systems is the feasibility of application to industrial level due to their investing and operating costs. Although first economic estimations are encouraging, the profitability of these systems has been demonstrated only at lab and pilot plant scale.

### Acknowledgements

Financial support from projects Consolider CSD2006-44, CTQ2008-00690/PPQ, ENE2010-15585, CTQ2008-03225/PPQ is gratefully acknowledged.

### REFERENCES

- Acevedo, C.R., Gardea-Torresdey, J.L., Tarquin, A.J., 2010. Silica removal from brine by using ion exchange. In: World Environmental and Water Resources Congress 2010: Challenges of Change – Proceedings of the World Environmental and Water Resources Congress.
- Ahmad, M., Williams, P., 2011. Assessment of desalination technologies for high saline brine applications – discussion paper. Desalination and Water Treatment 30, 22–36.
- Ahmed, M., Arakel, A., Hoey, D., Thumarukudy, M.R., Goosen, M.F.A., Al-Haddabi, M., Al-Belushi, A., 2003. Feasibility of salt production from inland RO desalination plant reject brine: a case study. Desalination 158, 109–117.
- Ahmed, M., Shayya, W.H., Hoey, D., Al-Handaly, J., 2001. Brine disposal from reverse osmosis desalination plants in Oman and the United Arab Emirates. Desalination 133 (2), 135–147.
- Ahmed, M., Shayya, W.H., Hoey, D., Mahendran, A., Morris, R., Al-Handaly, J., 2000. Use of evaporation ponds for brine disposal in desalination plants. Desalination 130 (2), 155–168.
- Altayaran, A.M., Madany, I.M., 1992. Impact of a desalination plant on the physical and chemical properties of seawater, Bahrain. Water Research 26 (4), 435–441.
- Al-Wazzan, Y., Safar, M., Mesri, A., 2003. Reverse osmosis brine staging treatment of subsurface water. Desalination 155 (2), 141–151.
- Arnal, J.M., Sancho, M., Iborra, I., Gozálvez, J.M., Santafé, A., Lora, J., 2005. Concentration of brines from RO desalination plants by natural evaporation. Desalination 182, 435–439.
- Badruzzaman, M., Oppenheimer, J., Adham, S., Kumar, M., 2009. Innovative beneficial reuse of reverse osmosis concentrate using bipolar membrane electrodialysis and electrochlorination processes. Journal of Membrane Science 326 (2), 392–399.
- Bagastyo, A.Y., Keller, J., Poussade, Y., Batstone, D.J., 2011a. Characterisation and removal of recalcitrants in reverse osmosis concentrates from water reclamation plants. Water Research 45 (7), 2415–2427.
- Bagastyo, A.Y., Keller, J., Batstone, D.J., 2011b. Size fractionation characterisation of removed organics in reverse osmosis concentrates by ferric chloride. Water Science and Technology 63 (9), 1795–1800.
- Benner, J., Salhi, E., Ternes, T., von Gunten, U., 2008. Ozonation of reverse osmosis concentrate: kinetics and efficiency of beta blocker oxidation. Water Research 42 (12), 3003–3012.
- Bond, R., Veerapaneni, S., 2008. Zeroing in on ZLD technologies for inland desalination. Journal American Water Works Association (AWWA) 100, 76–89.
- Chaplin, B.P., Schrader, G., Farrell, J., 2010. Electrochemical destruction of N-nitrosodimethylamine in reverse osmosis

concentrates using boron-doped diamond film electrodes. Environmental Science and Technology 44 (11), 4264–4269.

- Chelme-Ayala, P., Smith, D.W., El-Din, M.G., 2009. Membrane concentrate management options: a comprehensive critical review. Canadian Journal of Civil Engineering 36 (6), 1107–1119.
- Curcio, E., Ji, X., Di Profio, G., Sulaiman, A.O., Fontananova, E., Drioli, E., 2010. Membrane distillation operated at high seawater concentration factors: role of the membrane on CaCO<sub>3</sub> scaling in presence of humic acid. Journal of Membrane Science 346 (2), 263–269.
- Del Bene, J.V., Jirka, G., Largier, J., 1994. Ocean brine disposal. Desalination 97, 365–372.
- Dialynas, E., Mantzavinos, D., Diamadopoulos, E., 2008. Advanced treatment of the reverse osmosis concentrate produced during reclamation of municipal wastewater. Water Research 42 (18), 4603–4608.
- Einav, R., Lokiec, F., 2003. Environmental aspects of a desalination plant in Ashkelon. Desalination 156, 79–85.
- Ersever, I., Ravindran, V., Pirbazari, M., 2007a. Biological denitrification of reverse osmosis brine concentrates: I. Batch reactor and chemostat studies. Journal of Environmental Engineering and Science 6 (5), 503–518.
- Ersever, I., Ravindran, V., Pirbazari, M., 2007b. Biological denitrification of reverse osmosis brine concentrates: II. Fluidized bed adsorber reactor studies. Journal of Environmental Engineering and Science 6 (5), 519–532.
- Farooq, R., Shaukat, S.F., Khan, A.K., Farooq, U., 2008. Ultrasonic induced decomposition of methidathion pesticide. Journal of Applied Sciences 8 (1), 140–145.
- Gabelich, C.J., Rahardianto, A., Northrup, C.R., Yun, T.I., Cohen, Y., 2011. Process evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting. Desalination 272, 36–45.
- Gabelich, C.J., Xu, P., Cohen, Y., 2010. Chapter 10 concentrate treatment for inland desalting. Sustainability Science and Engineering 2, 295–326.
- Gabelich, C.J., Williams, M.D., Rahardianto, A., Franklin, J.C., Cohen, Y., 2007. High-recovery reverse osmosis desalination using intermediate chemical demineralization. Journal of Membrane Science 301, 131–141.
- Gilron, J., Folkman, Y., Savliev, R., Waisman, M., Kedem, O., 2003. WAIV – wind aided intensified evaporation for reduction of desalination brine volume. Desalination 158, 205–214.
- Greenlee, L.F., Testa, F., Lawler, D.F., Freeman, B.D., Moulin, P., 2011. Effect of antiscalant degradation on salt precipitation and solid/liquid separation of RO concentrate. Journal of Membrane Science 366, 48–61.
- Greenlee, L.F., Testa, F., Lawler, D.F., Freeman, B.D., Moulin, P., 2010a. Effect of antiscalants on precipitation of an RO concentrate: metals precipitated and particle characteristics for several water compositions. Water Research 44 (8), 2672–2684.
- Greenlee, L.F., Testa, F., Lawler, D.F., Freeman, B.D., Moulin, P., 2010b. The effect of antiscalant addition on calcium carbonate precipitation for a simplified synthetic brackish water reverse osmosis concentrate. Water Research 44 (9), 2957–2969.
- Greenlee, L.F., Lawler, D.F., Freeman, B.D., Marrot, B., Moulin, P., 2009. Reverse osmosis desalination: water sources, technology, and today's challenges. Water Research 43 (9), 2317–2348.
- Gryta, M., 2002. Concentration of NaCl solution by membrane distillation integrated with crystallization. Separation Science and Technology 37 (15), 3535–3558.
- Hajbi, F., Hammi, H., M'Nif, A., 2010. Reuse of RO desalination plant reject brine. Journal of Phase Equilibria and Diffusion 31 (4), 341–347.

- He, F., Gilron, J., Lee, H., Song, L., Sirkar, K.K., 2008. Potential for scaling by sparingly soluble salts in crossflow DCMD. Journal of Membrane Science 311, 68–80.
- Hoffmann, M.R., Hua, I., Höchemer, R., 1996. Application of ultrasonic irradiation for the degradation of chemical contaminants in water. Ultrasonics Sonochemistry 3 (3), S163–S172.
- Jegatheesan, V., Liow, J.L., Shu, L., Kim, S.H., Visvanathan, C., 2009. The need for global coordination in sustainable development. Journal of Cleaner Production 17 (7), 637–643.
- Jeppesen, T., Shu, L., Keir, G., Jegatheesan, V., 2009. Metal recovery from reverse osmosis concentrate. Journal of Cleaner Production 17 (7), 703–707.
- Ji, X., Curcio, E., Al Obaidani, S., Di Profio, G., Fontananova, E., Drioli, E., 2010. Membrane distillation-crystallization of seawater reverse osmosis brines. Separation and Purification Technology 71 (1), 76–82.
- Katzir, L., Volkmann, Y., Daltrophe, N., Korngold, E., Mesalem, R., Oren, Y., Gilron, J., 2010. WAIV – wind aided intensified evaporation for brine volume reduction and generating mineral byproducts. Desalination and Water Treatment 13, 63–73.
- Korngold, E., Aronov, L., Daltrophe, N., 2009. Electrodialysis of brine solutions discharged from an RO plant. Desalination 2428, 215–227.
- Korngold, E., Aronov, L., Belayev, N., Kock, K., 2005. Electrodialysis with brine solutions oversaturated with calcium sulfate. Desalination 172 (1), 63–75.
- Kumar, M., Badruzzaman, M., Adham, S., Oppenheimer, J., 2007. Beneficial phosphate recovery from reverse osmosis (RO) concentrate of an integrated membrane system using polymeric ligand exchanger (PLE). Water Research 41 (10), 2211–2219.
- Lattemann, S., Höpner, T., 2008. Environmental impact and impact assessment of seawater desalination. Desalination 220, 1–15.
- Le Dirach, J., Nisan, S., Poletiko, C., 2005. Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems. Desalination 182, 449–460.
- Lee, L.Y., Ng, H.Y., Ong, S.L., Hu, J.Y., Tao, G., Kekre, K., Viswanath, B., Lay, W., Seah, H., 2009a. Ozone-biological activated carbon as a pretreatment process for reverse osmosis brine treatment and recovery. Water Research 43 (16), 3948–3955.
- Lee, L.Y., Ng, H.Y., Ong, S.L., Tao, G., Kekre, K., Viswanath, B., Lay, W., Seah, H., 2009b. Integrated pretreatment with capacitive deionization for reverse osmosis reject recovery from water reclamation plant. Water Research 43 (18), 4769–4777.
- Macedonio, F., Katzir, L., Geisma, N., Simone, S., Drioli, E., Gilron, J., 2011. Wind-Aided Intensified eVaporation (WAIV) and membrane crystallizer (MCr) integrated brackish water desalination process: advantages and drawbacks. Desalination 273 (1), 127–135.
- Malaeb, L., Ayoub, G.M., 2011. Reverse osmosis technology for water treatment: state of the art review. Desalination 267 (1), 1–8.
- Malaxos, P.J., Morin, O.J., 1990. Surface water discharge of reverse osmosis concentrates. Desalination 78 (1), 27–40.
- Martinetti, C.R., Childress, A.E., Cath, T.Y., 2009. High recovery of concentrated RO brines using forward osmosis and membrane distillation. Journal of Membrane Science 331, 31–39.
- Mauguin, G., Corsin, P., 2005. Concentrate and other waste disposals from SWRO plants: characterization and reduction of their environmental impact. Desalination 182, 355–364.
- Mavrov, V., Chmiel, H., Heitele, B., Rogener, F., 1999. Desalination of surface water to industrial water with lower impact on the environment part 4: treatment of effluents from water

desalination stages for reuse and balance of the new technological concept for water desalination. Desalination 124, 205–216.

- Meerganz von Medeazza, G.L., 2005. "Direct" and socially-induced environmental impacts of desalination. Desalination 185, 57–70.
- Meneses, M., Pasqualino, J.C., Céspedes-Sánchez, R., Castells, F., 2010. Alternatives for reducing the environmental impact of the main residue from a desalination plant. Journal of Industrial Ecology 14 (3), 512–527.
- Mericq, J., Laborie, S., Cabassud, C., 2010. Vacuum membrane distillation of seawater reverse osmosis brines. Water Research 44 (18), 5260–5273.
- Mickley, M.C., 2006. Membrane Concentrate Disposal: Practices and Regulation. Report No.123. Bureau of Reclamation, Denver, CO, second ed. Water Treatment Engineering and Research Group; Mickley and Associates, Boulder, CO.
- Mickley, M.C., 2001. Membrane Concentrate Disposal: Practices and Regulation. Bureau of Reclamation, Denver, CO. Water Treatment Engineering and Research Group; Mickley and Associates, Boulder, CO.
- Mohammadesmaeili, F., Badr, M.K., Abbaszadegan, M., Fox, P., 2010a. Mineral recovery from inland reverse osmosis concentrate using isothermal evaporation. Water Research 44 (20), 6021–6030.
- Mohammadesmaeili, F., Badr, M.K., Abbaszadegan, M., Fox, P., 2010b. Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment. Water Environmental Research 82 (4), 342–350.
- Muniz, A., Skehan, S., 1990. Disposal of concentrate from brackish water desalting plants by use of deep injection wells. Desalination 78 (1), 41–47.
- Muñoz, I., Fernández-Alba, A.R., 2008. Reducing the environmental impacts of reverse osmosis desalination by using brackish groundwater resources. Water Research 42 (3), 801–811.
- Nathoo, J., Jivanji, R., Lewis, A.E., 2009. Freezing your brines off: eutectic freeze crystallization for brine treatment. In: International Mine Water Conference, pp. 431–437.
- Neilly, A., Jegatheesan, V., Shu, L., 2009. Evaluating the potential for zero discharge from reverse osmosis desalination using integrated processes – a review. Desalination and Water Treatment 11, 58–65.
- Ning, R.Y., Tarquin, A.J., 2010. Crystallization of salts from superconcentrate produced by tandem RO process. Desalination and Water Treatment 16, 238–242.
- Ning, R.Y., Tarquin, A.J., Balliew, J.E., 2010. Seawater RO treatment of RO concentrate to extreme silica concentrations. Desalination and Water Treatment 22, 286–291.
- Ning, R.Y., Troyer, T.L., 2009. Tandom reverse osmosis process for zero-liquid discharge. Desalination 237, 238–242.
- Ning, R.Y., Tarquin, A., Trzcinski, M., Patwardhan, G., 2006. Recovery optimization of RO concentrate from desert wells. Desalination 201, 315–322.
- Oren, Y., Korngold, E., Daltrophe, N., Messalem, R., Volkman, Y., Aronov, L., Weismann, M., Bouriakov, N., Glueckstern, P., Gilron, J., 2010. Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach. Desalination 261 (3), 321–330.
- Oren, Y., 2008. Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review). Desalination 228, 10–29.
- Pérez, G., Fernández-Alba, A.R., Urtiaga, A.M., Ortiz, I., 2010. Electro-oxidation of reverse osmosis concentrates generated in tertiary water treatment. Water Research 44 (9), 2763–2772.
- Qu, D., Wang, J., Wang, L., Hou, D., Luan, Z., Wang, B., 2010. Concentrating primary reverse osmosis concentrate by direct

contact membrane distillation. Water Science and Technology: Water Supply 10 (3), 403–410.

- Qu, D., Wang, J., Wang, L., Hou, D., Luan, Z., Wang, B., 2009. Integration of accelerated precipitation softening with membrane distillation for high-recovery desalination of primary reverse osmosis concentrate. Separation and Purification Technology 67 (1), 21–25.
- Radjenovic, J., Bagastyo, A., Rozendal, R.A., Mu, Y., Keller, J., Rabaey, K., 2011. Electrochemical oxidation of trace organic contaminants in reverse osmosis concentrate using RuO<sub>2</sub>/ IrO<sub>2</sub>-coated titanium anodes. Water Research 45 (4), 1579–1586.
- Rahardianto, A., McCool, B.C., Cohen, Y., 2010. Accelerated desupersaturation of reverse osmosis concentrate by chemically-enhanced seeded precipitation. Desalination 264 (3), 256–267.
- Randall, D.G., Nathoo, J., Lewis, A.E., 2011. A case study for treating a reverse osmosis brine using eutectic freeze crystallization-approaching a zero waste process. Desalination 266, 256–262.
- Reddy, S.T., Lewis, A.E., Witkamp, G.J., Kramer, H.J.M., van Soronsen, J., 2010. Recovery of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O from a reverse osmosis retentate by eutectic freeze crystallisation technology. Chemical Engineering Research and Design 88 (9), 1153–1157.
- Roberts, D.A., Johnston, E.L., Knott, N.A., 2010. Impacts of desalination plant discharges on the marine environment: a critical review of published studies. Water Research 44 (18), 5117–5128.
- Seigworth, A., Ludlum, R., Reahl, E., 1995. Case study: integrating membrane processes with evaporation to achieve economical zero liquid discharge at the Doswell combined cycle facility. Desalination 102, 81–86.
- Singh, R., 2009. Brine recovery at industrial RO plants: conceptual process design studies. Desalination and Water Treatment 8, 54–67.
- Solley, D., Gronow, C., Tait, S., Bates, J., Buchanan, A., 2010. Managing the reverse osmosis concentrate from the Western Corridor recycled water scheme. Water Practice and Technology 5, 1–8.
- Squire, D., 2000. Reverse osmosis concentrate disposal in the UK. Desalination 132, 47–54.
- Squire, D., Murrer, J., Holden, P., Fitzpatrick, C., 1997. Disposal of reverse osmosis membrane concentrate. Desalination 108, 143–147.
- Stanford, B.D., Leising, J.F., Bond, R.G., Snyder, S.A., 2010. Chapter 11 inland desalination: current practices, environmental

implications, and case studies in Las Vegas, NV. Sustainability Science and Engineering 2, 327.

- Strathmann, H., 2010. Electrodialysis, a mature technology with a multitude of new applications. Desalination 264 (3), 268–288.
- Tang, W., Ng, H.Y., 2008. Concentration of brine by forward osmosis: performance and influence of membrane structure. Desalination 224, 143–153.
- Turek, M., Was, J., Dydo, P., 2009. Brackish water desalination in RO-single pass EDR system. Desalination and Water Treatment 7, 263–266.
- Urtiaga, A.M., Gorri, E.D., Ruiz, G., Ortiz, I., 2001. Parallelism and differences of pervaporation and vacuum membrane distillation in the removal of VOCs from aqueous streams. Separation and Purification Technology 22–23, 327–337.
- Van Der Bruggen, B., Lejon, L., Vandecasteele, C., 2003. Reuse, treatment, and discharge of the concentrate of pressuredriven membrane processes. Environmental Science and Technology 37 (17), 3733–3738.
- Van Hege, K., Verhaege, M., Verstraete, W., 2004. Electro-oxidative abatement of low-salinity reverse osmosis membrane concentrates. Water Research 38 (6), 1550–1558.
- Van Hege, K., Verhaege, M., Verstraete, W., 2002. Indirect electrochemical oxidation of reverse osmosis membrane concentrates at boron-doped diamond electrodes. Electrochemistry Communications 4, 296–300.
- Voutchkov, N., 2011. Overview of seawater concentrate disposal alternatives. Desalination 273, 205–219.
- Watson, I., 1990. Characterization of desalting concentrates. Desalination 78, 5–9.
- Westerhoff, P., Moon, H., Minakata, D., Crittenden, J., 2009. Oxidation of organics in retentates from reverse osmosis wastewater reuse facilities. Water Research 43, 3992–3998.
- Zhang, Y., Ghyselbrecht, K., Meesschaert, B., Pinoy, L., Van der Bruggen, B., 2010. Electrodialysis on RO concentrate to improve water recovery in wastewater reclamation. Journal of Membrane Science. doi:10.1016/j.memsci.2010.10.036.
- Zhang, Y., Van der Bruggen, B., Pinoy, L., Meesschaert, B., 2009. Separation of nutrient ions and organic compounds from salts in RO concentrates by standard and monovalent selective ionexchange membranes used in electrodialysis. Journal of Membrane Science 332, 104–112.
- Zhou, T., Lim, T.-T., Chin, S.-S., Fane, A.G., 2011. Treatment of organics in reverse osmosis concentrate from a municipal wastewater reclamation plant: feasibility test of advanced oxidation processes with/without pretreatment. Chemical Engineering Journal 166 (3), 932–939.