Valorisation of precipitated silica wastewater: pre-industrial scale results & replicability studies at lab-scale

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LIFE ZEROSILIBRINE project is a PILOT PROJECT to apply an innovate technology for the treatment of the wastewater (WW) generated during the production of precipitated silica, an environmental challenge with no feasible current solution.

The main objective of the project is to demonstrate a circular economy-oriented process based on membrane filtration (ultrafiltration (UF) and reverse osmosis (RO)) and evaporation-crystallization at pre-industrial scale (40 m^3/h) to recover water and anhydrous sodium sulphate from precipitated silica wastewater.

The production process of precipitated silica generates as a by-product a high conductivity saline stream that is discharged into natural channels after passing through WW treatment plants. In the production of precipitated silica, the main salt generated is sodium sulphate (Na_2SO_4) that must be separated from the product by washing, generating a high consumption of water. For each ton of precipitated silica produced, 0.75 tons of Na_2SO_4 are generated as a by-product in a discharge of 40 m^3 of saline effluent

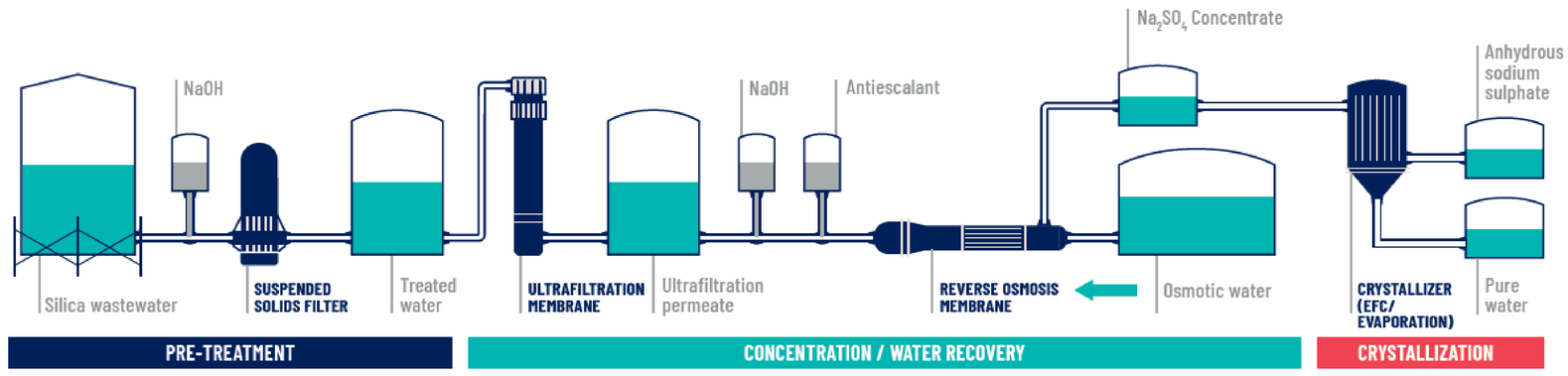


Figure 1. Process for the treatment of precipitated silica wastewater

Materials & Methods

Pre-industrial pilot at IQE

IQE constructed a pre-industrial membrane filtration pilot plant with capacity of treating 40 m^3/h of silica WW, consisting of a pretreatment with a suspended solids filter followed by an ultrafiltration (UF) step and two stages of reverse osmosis (RO) to concentrate de effluent. The aim of the concentration step is to concentrate the effluent up to 120 g/L of Na_2SO_4 before entering the following process step based on evaporation and crystallization. For the evaporation-crystallization step, IQE has constructed a unit with 1-2 m^3/h of evaporation capacity, based on a forced circulation evaporator (mechanical compression mechanism) followed by crystallization. The aim of the evaporation process is to reach feeding concentration for the crystallization step (around 250 g/L of Na_2SO_4), and in the crystallization step the sodium sulphate concentration will reach 960 g/L (96-97% sodium sulphate concentration). The post crystallization stages (wash column, centrifuge, and pre-pack drying) will be outsourced to providers with facilities to produce anhydrous sodium sulphate.

Figure 2. Construction process of the pre-industrial pilot at IQE

Figure 3. UF and RO pilot installations at IQE

Replicability & transferability studies at lab-scale

The solution proposed in LIFE ZEROSILIBRINE is being tested at laboratory scale in Eurecat with saline WW from other industrial sectors, to assess the replicability and transferability potential of the solution. Companies from different industrial sectors were contacted to invite them to participate in the replicability study. By now, the concentration step based on UF followed by RO has been tested at lab-scale successfully with 3 other WW from the food, chemical and textile industry. UF pretreatment was performed with a tubular T-CUT 100 kDa UF membrane (P: 1 bar, T: Room temperature). Reverse osmosis experiments were carried out in a lab-scale set-up for membrane testing that consists of thermostatic bath, a pump, a membrane testing cell for flat-sheet cupons and a jacketed reactor that contains de feed and to which the concentrate is recirculated. Tests were carried out at 25 ºC using BWRO-30XFR or BWRO-30XFRLE (Dupont-Filmtec) flat-sheet membrane cupons (0.014 m^2).

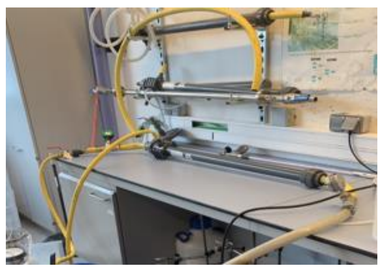
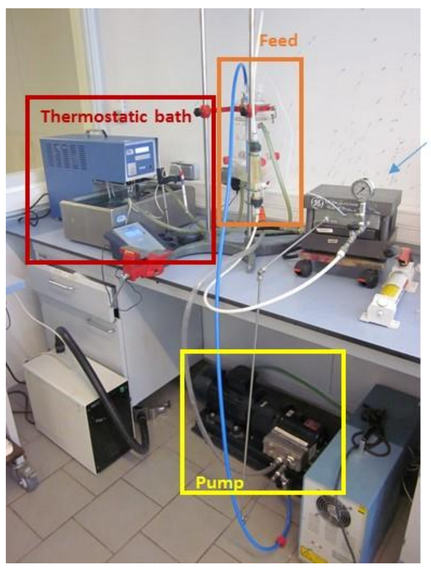
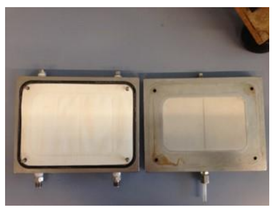


Figure 4. Tubular UF membrane set-up at lab scale





Flat-sheet membrane module

Figure 5. Set-up for RO tests at lab-scale

Results

Pre-industrial pilot at IQE

The reverse osmosis plant has been operating for around 1 year, and the evaporation-crystallization unit started to operate in June 2024 . Average operational data and flow compositions of the pre-industrial RO plant are presented in Table 1. Average recoveries in stage 1 and 2 result in a total average recovery of 85%.

Table 1. Characterizations of the flows and operation data of the pre-industrial RO plant

	Conductivity Feed [mS/cm]	Na_2SO_4 Feed [g/L]	Conductivity Concentrate [mS/cm]	Na_2SO_4 Concentrate [g/L]	Operation Pressure [bar]	Feed flow [m^3/h]	Recovery [%]
RO stage 1	26.5	20.6	61.1	63.7	32	40	69
RO stage 2	61.1	63.7	80	96.7	56	21	52

Replicability studies at lab-scale

Table 2 presents the results of the lab-scale test performed in the replicability and transferability study.

Table 2. Results of the replicability study at lab-scale (concentration step, UF+RO)

Industry	Origin of the WW	Main salt in the WW	Aim of applying the membrane concentration step	Main results (RO step)				
Wastewater from food industry	Production of casings for meat products (TSS: < 5 mg/L, EC: 7.8 mS/cm)	Na_2SO_4 (8,500 ppm)	Concentration for subsequent evaporation and crystallization of sodium sulphate and water recovery.	RO recovery : 80%	RO Operation pressure: 15-30 bar	RO average flux: 26.2 LMH	Rejection NH_4^+ :78%	Rejection NO_3^- :65%
Wastewater from chemical industry	Production of industrial gases (TSS: < 3 mg/L, EC: 27.7 mS/cm)	NH_4NO_3 (13,350 ppm)	Concentration for subsequent use as concentrated fertiliser and water recovery	RO recovery : 76%	RO Operation pressure: 30 bar	RO average flux: 27.7 LMH	Rejection Na^+: 96%	Rejection SO_4^{2-} :96%
Wastewater from textile industry	Dyeing process, bleaching and washing (TSS < 1 mg/L, EC: 6 mS/cm)	NaCl (2,780 ppm)	Colour removal and water recovery	RO recovery : 80%	RO Operation pressure: 12 bar	RO average flux: 24.5 LMH	Rejection Na^+: 97.3%	Rejection Cl^-: 97.5%

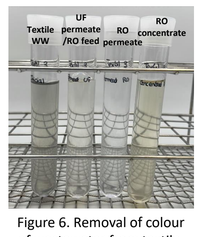


Figure 6. Removal of colour of wastewater from textile industry by applying the membrane concentration step at lab scale (UF+ RO)

Conclusions

The promising results obtained by now indicate that the technology demonstrated by LIFE ZEROSILIBRINE project can allow to achieve circular economy models for precipitated silica wastes as well as saline effluent from other industries. Efforts are currently focused on the start-up and operation of the evaporation-crystallization unit to obtain high quality anhydrous sodium sulphate, and on the optimisation of the UF-RO plant to achieve higher Na2SO4 concentrations (up to 120 g/L). Also, further experiments are being carried out at lab-scale in the frame of the replicability study, to test the technology on effluents from other industries.

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